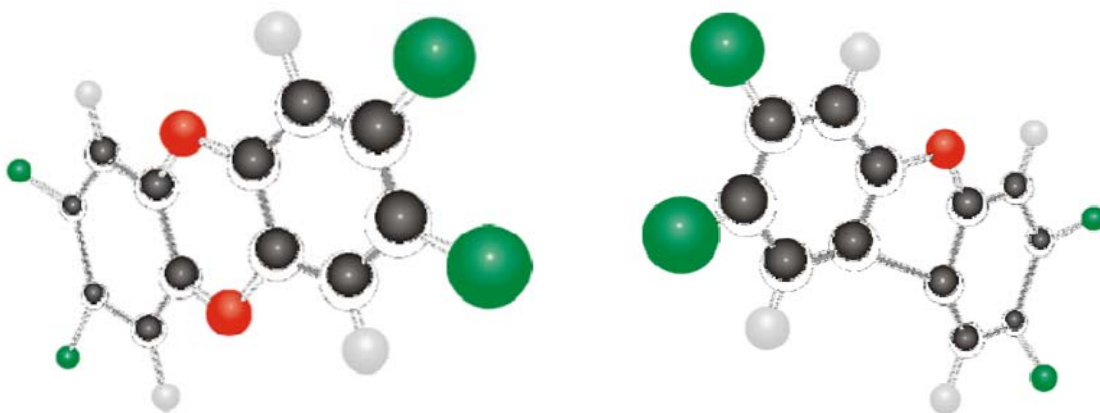




# Toolkit



**for Identification and Quantification  
of Releases of Dioxins, Furans and  
Other Unintentional POPs**

**under Article 5 of the Stockholm Convention**

January 2013

**This publication is intended to assist countries to establish release inventories of polychlorinated dibenzo-*p*-dioxins and dibenzofurans at a national or regional level. The information contained in this report comes from published scientific literature, government reports, Internet sources, and through personal communication. The designations employed and the presentations in this document do not imply any expression of opinion on behalf of UNEP or contributory organizations. UNEP or contributory organizations cannot be liable for misuse of the information contained in this publication.**

## **PREFACE**

One of the major goals of the Stockholm Convention on Persistent Organic Pollutants (POPs) is the continuing minimization and, where feasible, ultimate elimination of unintentionally produced POPs. Parties are required to identify, characterize, quantify and prioritize sources of releases of unintentionally produced POPs, and develop strategies with concrete measures, timelines and goals to minimize or eliminate these releases.

To support Parties in meeting these obligations, a methodology has been developed to ensure that source inventories and release estimates are complete, transparent, as well as consistent in format and content. It allows Parties to compare results, identify priorities, mark progress and follow changes over time at the national, regional and global levels.

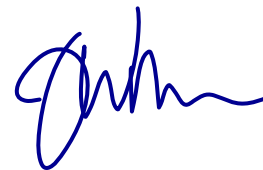
The Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases was first published in 2003 and revised in 2005. In 2006, the Conference of the Parties to the Stockholm Convention welcomed the second Toolkit edition and recognized its usefulness. At the same time, Parties acknowledged the need for its ongoing revision and updating, placing emphasis on key sources for which limited data were available and on providing support to developing countries in their efforts to verify their emission factors. Parties also requested overall improvement of the usefulness and user friendliness of the Toolkit.

The revision process was open and inclusive, involving experts nominated by Parties as well as by nongovernmental organizations and industry associations, and in cooperation with UNEP Chemicals.

The Toolkit is the most comprehensive available compilation of emission factors for all relevant PCDD/PCDF sources. It is useful particularly in countries where measurement data are limited, enabling the elaboration of source inventories and release estimates by using the default emission factors. It is also useful in countries where national measurement data are available, as a reference document for data comparison and validation purposes.

The Conference of the Parties at its fifth meeting in 2011 welcomed these revisions and updates, and Parties were encouraged to use the additional guidance.

This edition of the Toolkit contains all new information, as well as model inventories illustrating relevant processes. In addition, the entire Toolkit is now available in an interactive electronic version, with information structured according to the level of technical detail. With these improvements, we hope the Parties will find the new Toolkit edition more useful and user friendly than ever.



Jim Willis  
Executive Secretary

## ACKNOWLEDGEMENTS

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All experts nominated by parties and others, included in the Toolkit Expert Roster, were involved in the Toolkit review and updating process at least by electronic means. The following experts are gratefully acknowledged for their substantial contribution to the development of this document.

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## Abbreviations and Acronyms

2,4,5-T	2,4,5-Trichlorophenoxyacetic acid
°C	Degrees Celsius
a	Year (annum), 365 days
ADt	Air-dried ton (of pulp)
APC(S)	Air pollution control (system)
BAT	Best available techniques
BEP	Best environmental practices
BF	Blast furnace
BOF	Basic oxygen furnace
BOS	Basic oxygen steel
C	Chlorination bleaching stage using molecular chlorine dispersed dissolved in water (pulp and paper production)
CCMS	Committee on Challenges of Modern Society
CHP	Combined heat and power
CF	Cupola furnace
CLRTAP	Convention on Long-range Transboundary Air Pollution
CNP	2,4,6-Trichlorophenyl-4'-nitrophenyl ether
COCHILCO	Comisión Chilena del Cobre (Chilean Copper Commission)
CORINAIR	Core inventory of air emissions
CTMP	Chemo-thermo-mechanical pulp
CUF	Capacity Utilization Factor
D	Chlorine dioxide bleaching stage using a water solution of chlorine dioxide (ClO <sub>2</sub> ) (Section on pulp and paper production)
DCB	Dichlorobenzene
dl-PCB	dioxin-like Polychlorinated Biphenyls
DL	Detection limit
d.m.	Dry matter
E	Extraction bleaching stage using sodium hydroxide (NaOH)
EAF	Electric arc furnace
ECF	Elemental chlorine free (bleaching)

ECVM	European Council of Vinyl Manufacturers
EDC	1,2-Dichloroethane
EMEP	Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe
EPA	Environmental Protection Agency
ESP	Electrostatic precipitator
EU	European Union
FAO	Food and Agriculture Organization
GDP	Gross Domestic Product
GEF	Global Environment Facility
h	Hour(s)
H <sub>2</sub> SO <sub>4</sub>	Sulfuric acid
ha	Hectare(s)
HCB	Hexachlorobenzene
HW	Hazardous waste
I-TEF	International Toxicity Equivalency Factor
I-TEQ	International Toxic Equivalent
IF	Induction furnace
IPCS	International Programme on Chemicals Safety (of the World Health Organisation)
IPPC	Integrated Pollution Prevention and Control (of the European Union)
ISO	International Organization for Standardization
K	(Degree) Kelvin
kPa	Kilo Pascal (= one thousand Pascal)
L	Liter
LPG	Liquefied petroleum gas
LOI	Loss of ignition (a measure for residual carbon content)
LoC	Level of Confidence
LOQ	Limit of quantification
LPG	Liquefied petroleum gas
LS	Liquid steel

m	Meter
m <sup>3</sup>	Cubic meter (typically under operating conditions without normalization to, <i>e.g.</i> , temperature, pressure, humidity)
Mg	Magnesium but see also: megagram (under units)
MSW	Municipal solid waste
NA	Not applicable (not a relevant release vector)
NaOH	Sodium hydroxide
Na <sub>2</sub> S	Sodium sulfide
NATO	North Atlantic Treaty Organization
NCASI	National Council (of the Paper Industry) for Air and Steam Improvement, Inc.
N-TEQ	Toxic equivalent using the Nordic scheme (commonly used in the Scandinavian countries)
ND	Not determined/no data (in other words: so far, no measurements available)
NFR	Nomenclature For Reporting
NIP	National Implementation Plan (under the Stockholm Convention on Persistent Organic Pollutants)
Nm <sup>3</sup>	Normalized (standard) cubic meter; the volume a gas occupies at atmospheric pressure (1,013 mbar) and 273.15 K (0°C)
<i>o</i>	ortho
O	Oxygen bleaching stage (pulp and paper production)
OECD	Organisation for Economic Co-operation and Development
OSPAR	Commission for the Protection of the Marine Environment of the North-East Atlantic
<i>p</i>	para
PARCOM	Paris-Oslo Commission
PCB	Polychlorinated biphenyls
PCDD	Polychlorinated dibenzo- <i>p</i> -dioxins
PXDD	Polyhalogenated dibenzo- <i>p</i> -dioxins
PCDF	Polychlorinated dibenzofurans
PXDF	Polyhalogenated dibenzofurans
PeCBz	Pentachlorobenzene

PCP	Pentachlorophenol
PCP-Na	Sodium pentachlorophenol
POPs	Persistent organic pollutants
PRTR	Pollutant Release and Transfer Register
PTS	Persistent toxic substances
PVC	Polyvinyl chloride
RDF	Refuse derived fuel
rpm	Revolutions per minute
SCR	Selective catalytic reduction/reaction
SI	International system of units
SNAP	Selected Nomenclature for Air Pollution
t	Ton (metric)
TCB	Trichlorobenzene
TCF	Totally chlorine free (bleaching)
TEF	Toxicity Equivalency Factor
TEQ	Toxic Equivalent
	Note: For the purpose of the Toolkit, there is no difference if concentrations or emission factors are reported in I-TEQ or N-TEQ or WHO-TEQ (for PCDD/PCDF only)
TMP	Thermo-mechanical pulp
TRI	Toxics Release Inventory
UNCED	United Nations Conference on Environment and Development
UNDP	United Nations Development Programme
UNECE	United Nations Economic Commission for Europe
UNEP	United Nations Environment Programme
UNIDO	United Nations Industrial Development Organization
URL	Uniform Resource Locator (the global address of documents and other resources on the World Wide Web)
UV	Ultra-violet
VCM	Vinyl chloride monomer
VSK	Vertical shaft kilns

WEC	World Energy Council
WHO	World Health Organization

## Units

### SI Units

g	gram	$10^0$ g	
kg	kilogram	$10^3$ g	
t	ton	$10^6$ g (1,000 kg)	also Mg Megagram
kt	kilo-ton	1,000 t	
mg	milligram	$10^{-3}$ g	
µg	microgram	$10^{-6}$ g	
ng	nanogram	$10^{-9}$ g	
pg	picogram	$10^{-12}$ g	
fg	femtogram	$10^{-15}$ g	

kJ	Kilojoule	$10^3$ Joule
MJ	Megajoule	$10^6$ Joule
GJ	Gigajoule	$10^9$ Joule
TJ	Terajoule	$10^{12}$ Joule

MW	Megawatt
MWh	Megawatt hour

Pa	Pascal
kPa	kilopascal $10^3$ Pascal

### Non-SI Units

Gallon	1 gal = 0.1337 ft <sup>3</sup> = 0.0038 m <sup>3</sup>
pound	1 lb. = 0.4536 kg
inch	1 in = 2.54 cm = 0.0254 m

### Definitions

Unintentional POPs Throughout the document, the term “unintentional POPs” will be used to address the persistent organic pollutants that are listed in Annex C Part I of the Stockholm Convention.

## **PART I GENERAL GUIDANCE**

### **Chapter 1 Introduction and Overview**

Under the Stockholm Convention on Persistent Organic Pollutants (POPs), Parties are required to reduce total releases from anthropogenic sources of the chemicals listed in Annex C with the goal of continually minimizing and, where feasible, ultimately eliminating releases of these unintentionally produced chemicals. Toward this end, Parties must develop action plans as part of their National Implementation Plans (NIP) to identify, characterize and address the releases of unintentional POPs listed in Annex C. Action plans to be developed according to Article 5 of the Convention shall include evaluations of current and projected releases that are derived through the development and maintenance of source inventories and release estimates, taking into consideration the source categories listed in Annex C.

To achieve the goal of the Convention, Parties are required to implement or promote best available techniques (BAT) and best environmental practices (BEP), as described in the “Guidelines on Best Available Techniques and Provisional Guidance on Best Environmental Practices relevant to Article 5 and Annex C of the Stockholm Convention on Persistent Organic Pollutants”.

Five years after developing their action plan, Parties are required to review their adopted strategies, including the extent to which their unintentional POPs releases have been reduced, and to incorporate such reviews in national reports pursuant to Article 15.

#### **1.1 Chemicals Listed in Annex C**

Pursuant to Article 5 of the Convention, the following unintentional POPs are listed in Annex C:

- Polychlorinated dibenzo-*p*-dioxins (PCDD)
- Polychlorinated dibenzofurans (PCDF),
- Polychlorinated biphenyls (PCB),
- Hexachlorobenzene (HCB), and
- Pentachlorobenzene (PeCBz).<sup>1</sup>

Among these, PCDD and PCDF (also collectively referred to as PCDD/PCDF) have never been used as commercial products, nor were intentionally manufactured for any reason other than laboratory purposes. PCB, HCB and PeCBz are also unintentionally formed, usually from the same sources that produce PCDD/PCDF. However, unlike PCDD/PCDF, they have also been manufactured and used for specific purposes, their intentional production and use being by far higher than the unintentional formation and release.

PCDD/PCDF releases are accompanied by releases of other unintentional POPs, which can be minimized or eliminated by the same measures that are used to address PCDD/PCDF releases. When a

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<sup>1</sup> Annex C was amended to include pentachlorobenzene at the fourth meeting of the Conference of Parties, held from 4 to 8 May 2009, by decision SC-4/16.

comprehensive inventory of PCDD/PCDF is elaborated, it allows to identify priority sources, set measures and develop action plans to minimize releases **of all unintentional POPs**.

It is thus recommended, for practical reasons, that inventory activities be focused on PCDD/PCDF, as these substances are **indicative of the presence of other unintentional POPs**. They are considered to constitute a sufficient basis for **identifying** and **prioritizing** sources of all such substances as well as for **devising applicable control measures for all Annex C POPs** and for **evaluating their efficacy**.

Only in the context of research or other projects it is advisable to analyze emissions of all unintentional POPs listed in Annex C in order to produce useful information for the purpose of deriving emission factors.

In addition to emission factors for PCDD/PCDF, the Toolkit also contains emission factors for other POPs when such information is available. Typically, emission factors are provided for the five release vectors, *i.e.*, air ( $EF_{Air}$ ), water ( $EF_{Water}$ ), land ( $EF_{Land}$ ), product ( $EF_{Product}$ ), and residue ( $EF_{Residue}$ ).

## 1.2 Purpose

The purpose of the “Toolkit for Identification and Quantification of Releases of Dioxins, Furans, and Other Unintentional POPs” is to support Parties in preparing PCDD/PCDF inventories<sup>2</sup> that are consistent in format and content, ensuring that it is possible to compare results, identify priorities, mark progress and follow changes over time at the country level, and at the regional and global levels. Towards this end, the Toolkit provides the following “tools”:

- A simple but comprehensive procedure for identifying sources of PCDD/PCDF, including but not limited to the source categories listed in Annex C, Parts II and III;
- Guidance on gathering basic information on the design, operation and/or expected performance of sources that supports their classification and the assignment of appropriate default emission factors;
- Default emission factors – values for the quantity of PCDD/PCDF, expressed as TEQ, released to each vector per unit of activity (*e.g.*,  $\mu\text{g TEQ}$  per ton of material produced, per ton of fuel burned, etc.) that have been assigned for each class within the source categories. For the other unintentional POPs, mass concentrations will be assigned as appropriate;
- Guidance on acquiring data and related information to estimate national values for annual activity rates for source categories and/or classes within source categories, *e.g.*, tons per year of waste burned, tons per year of feed material processed, tons per year of product produced, etc.; and
- A spreadsheet to list all source groups, source categories and their associated classes and emission factors, for the five release vectors. This spreadsheet will automatically calculate annual PCDD/PCDF releases from all source categories in a given country or region where national activity data are entered.

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<sup>2</sup> In this document, the terms “inventory” and “inventories” are used to include both source inventories and the associated release estimates.



The emission factors can be modified in the spreadsheet, *i.e.*, countries may use their own emission factors instead of the default ones, preferably using the same units to ensure comparability of results. Countries can also insert new source categories or classes by adding extra lines into the worksheet to better reflect national circumstances.

### 1.3 Structure and Use of the Toolkit

The Toolkit is divided into three parts: Part I contains four chapters providing general guidance for inventory development, Part II contains default emission factors for nine of the ten source groups, and Part III provides complementary information, including 53 annexes and 11 example inventories.

#### Part I

**Chapter 1- Introduction and Overview** summarizes the obligations of Parties under Article 5 and Annex C of the Stockholm Convention, describes the purpose and structure of the Toolkit and the chemicals listed in Annex C, including a brief overview of their formation and sources.

**Chapter 2- Identification of PCDD/PCDF Sources and Estimation of Releases** addresses the identification of sources and provides general guidance on gathering information that will allow for 1) sources to be identified and catalogued according to the source category and class to facilitate the selection of the most appropriate default emission factors, and 2) guidance to determine activity rates for each of the classes within each source category.

**Chapter 3- Reporting of releases** explains how to undertake inventory updates and revisions as well as projections of future releases. Finally, the reporting format under Article 15 of the Convention is described.

**Chapter 4- Data quality** provides information on the inventory data quality criteria along with guidance on possible quality assurance and quality control measures and a simple approach to characterize the quality of the inventory results.

#### Part II

**1 – Waste Incineration** addresses seven source categories of waste incinerators, the classes within each category and the default emission factors for each class.

**2 – Ferrous and Non-Ferrous Metal Production** addresses twelve source categories for the production of metals and metal alloys including recycling operations, the classes within each category and the default emission factors for each class.

**3 – Heat and Power Generation** addresses five source categories of large and small installations using fossil fuels, biomass or gas, the classes within each category and the default emission factors for each class.

**4 – Production of Mineral Products** addresses seven source categories of processes to manufacture mineral products, the classes within each category and the default emission factors for each class.

**5 – Transport** addresses four source categories including road and ship transport, the classes within each category and the default emission factors for each class.

**6 – Open Burning Processes** addresses two source categories of burning biomass or waste without technical equipment, the classes within each category and the default emission factors for each class.

**7 – Production and Use of Chemicals and Consumer Goods** addresses eight source categories of various industrial activities, the classes within each category and the default emission factors for each class.

**8 – Miscellaneous** addresses an array of five source categories that do not match the description of any other source group, the classes within each category and the default emission factors for each class.

**9 – Disposal and Landfill** addresses five source categories related to waste disposal, the classes within each category and the default emission factors for each class.

**10 – Contaminated Sites and Hotspots** addresses thirteen source categories that should only be noted in the inventory, where possible, since these categories cannot be further classified and no default emission factors can be provided.

### **Part III**

The following annexes provide complementary information:

**Annex 1 - Table of TEFs**

**Annex 2 - Guidance on identifying sources of PCDD/PCDF**

**Annex 3 - Questionnaires**

**Annex 4 - Compilation of all emission factors**

**Annex 5 - Reporting of releases**

**Annex 6 - Usage of units in air emissions**

**Annex 7 - Per capita/GDP emissions**

**Annex 8 - Data quality**

**Annexes 9 to 53** provide complementary information to source groups 1-10 and the source categories included in the respective groups.

Eleven **example inventories** are also included in Part III to illustrate the process of update and revision of inventories, as well as specific examples of inventories for source groups 1-10.

The Toolkit (current version updating and amending edition 2, which was published in 2005) is presented in an electronic version (web-based and CD-ROM). The electronic version of the Toolkit has been developed to increase the availability, portability and storage of the information. It delivers the Toolkit's content in an interactive and dynamic manner. The information is organized in a user-friendly multi-layer structure according to the level of complexity, where information elements are arranged according to the relevance for the inventory process:

- The first layer contains key elements of the Toolkit and essential information for the development of the inventory;
- The second layer of complementary information or additional explanatory material is included in annexes and example inventories accessible via hyperlinks;
- Further complementary information is accessible via pop-up windows;
- Cross-referencing within the Toolkit sections is done via internal links; and
- External links are used to reference outside resources.

Among other features, the web-based tool also offers access to interactive features including a search tool and access to Excel files for calculating releases. The user is therefore given flexibility in accessing the content of the Toolkit to meet specific information requirements.

## **1.4 POPs Releases from Sources**

The Toolkit has been assembled for the purpose of assisting each country in identifying and quantifying sources of unintentional POPs that are located within the country's borders and estimating releases from those sources.

Sources of POPs releases are of four general types, three of which are active, ongoing processes, and one is a legacy of historic activities:

- Chemical production processes, *e.g.*, facilities or production units that produce chlorinated phenols or in which certain other chlorinated chemicals are manufactured, or that produce pulp and paper using elemental chlorine for chemical bleaching;
- Thermal and combustion processes, *e.g.*, waste incineration, combustion of solid and liquid fuels, or production of metals in thermal processes;
- Biogenic processes in which PCDD/PCDF may be formed from precursors – manufactured chemicals such as pentachlorophenol that are structurally closely related precursors of PCDD/PCDF.
- Reservoir sources such as historic dumps containing PCDD/PCDF and other POPs-contaminated wastes, and soils and sediments in which POPs have accumulated over time.

The Toolkit presents information on each of the unintentional POPs source categories listed in Annex C, some additional source categories, and a strategy for identifying new source categories. It describes a step-by-step process to estimate PCDD/PCDF releases from each source category to the following environmental media:

- Air,
- Water (surface and ground water, including marine and estuarine water), and
- Land (surface soils),

and to these process outputs:

- Products (such as chemical formulations, including pesticides or consumer goods such as paper, textiles, etc.);
- Residues (including certain liquid wastes, sludge, and solid residues, which are handled and disposed of as waste or may be recycled).

### **Combustion Processes**

PCDD/PCDF and other unintentional POPs can be formed in combustion processes when their component elements – carbon, oxygen, hydrogen, and chlorine – are present and combustion temperatures range between 200°C and 900°C (De Fre and Rymen 1989). Two primary mechanisms for PCDD/PCDF formation during combustion have been proposed:

- *De novo* formation, in which non-extractable carbon-based structures that fundamentally differ from the PCDD/PCDF undergo transformations and reactions to form PCDD/PCDF; and
- Precursor formation/reactions in which hydrocarbon fragments undergo cyclization or incomplete oxidation to form chemicals that share structural similarities with PCDD/PCDF and that undergo further reactions to finally form PCDD/PCDF.

PCDD/PCDF formation *via* these mechanisms can take place homogeneously (molecules react entirely in the gas phase or in the solid phase) or heterogeneously (the reactions take place between gas phase molecules and surfaces).

PCDD/PCDF can also be destroyed during combustion when temperatures are sufficiently high, residence times are adequate and mixing in the combustion zone is sufficiently thorough.<sup>3</sup> However, combustion gases must also be rapidly cooled in the post-combustion zone in order to minimize the formation of new PCDD/PCDF in this phase. Variables known to influence PCDD/PCDF formation in combustion processes include the following:

- Technology: Poor combustion, poor mixing in the combustion chamber, poorly designed and managed post-combustion chambers, and inadequate air pollution control devices are associated with increased PCDD/PCDF formation.
- Temperature: Formation has been reported in post-combustion zones and air pollution control devices at temperatures ranging from 200°C to 650°C, with the greatest formation occurring between 200°C and 450°C and peaking at about 300°C;
- Metals: Formation is catalyzed by metals including copper, iron, zinc, aluminum, chromium, and manganese;
- Sulphur and nitrogen: Chemicals containing sulphur and nitrogen have the potential to inhibit the formation of PCDD/PCDF in certain conditions, but may give rise to other undesirable by-products;

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<sup>3</sup> Good combustion practices include presence of the “3 Ts” – temperature, turbulence, and time of residence.

- Chlorine: Chlorine must be present. Whether chlorine is present as organic, inorganic or elemental in the materials combusted is relatively negligible. However, its presence in fly ash or in its elemental form in the gas phase may be especially important.

Other variables and combinations of conditions also affect PCDD/PCDF formation. For example, while simulating the burning of household waste in a metal barrel inside a burn hut, Gullet *et al.* (1999) reported greater PCDD/PCDF formation with 1) increased chlorine in the waste, independent of the original form of the chlorine – organic or inorganic; 2) higher humidity; 3) increased waste load; and 4) higher levels of catalytic metals.

### ***Industrial-Chemical Processes***

As with combustion processes, carbon, hydrogen, oxygen, and chlorine must also be present for PCDD/PCDF to form in industrial-chemical processes. In chemical manufacturing processes, PCDD/PCDF formation may be favored if one or more of the following conditions apply (NATO/CCMS 1992, Hutzinger and Fiedler 1988):

- Elevated temperatures (>150°C);
- Alkaline conditions (especially during purification);
- Metal catalysis;
- Ultraviolet radiation or substances that generate radicals.

Among chlorine-containing chemicals, the following groups have been associated with the formation of PCDD/PCDF as byproducts during their production:

- Chlorinated phenols and their derivatives,
- Chlorinated aromatics and their derivatives,
- Chlorinated aliphatic chemicals,
- Chlorinated catalysts and inorganic chemicals.

PCDD/PCDF can be also formed as byproducts of some chemicals that do not contain chlorine when some form of chlorine is present or used during their production.

### ***Application of Toxic Equivalents (TEQ)***

Taken as a whole, PCDD and PCDF are a group of 210 tricyclic, chlorine-containing aromatic chemicals; there are 75 congeners of PCDD and 135 congeners of PCDF possible. PCDD and PCDF typically occur as mixtures. The most toxic compounds have chlorines in the 2, 3, 7 and 8 positions; they have been assigned a toxicity equivalency factor (TEF) based on the relative potency of each congener in comparison to the most toxic congener, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. In total, there are 17 congeners in which chlorine atoms occur at the 2, 3, 7, and 8 positions. Mixtures of these congeners are often evaluated and reported as a single number called toxic equivalent (TEQ). To determine the TEQ of a mixture, the mass concentration of each congener is analytically determined, multiplied with the assigned TEF, and the products summed. The first scheme, derived by the Committee on the Challenges of Modern Society of the North Atlantic Treaty Organization in 1988 and called I-TEFs, covered 17

PCDD/PCDF. Subsequent revisions of TEFs have been coordinated by the World Health Organization (WHO) in 1997 and 2005. These revisions also included 12 dioxin-like polychlorinated biphenyls (dl-PCB). For PCB, the compounds having the highest toxicity are those in which the molecule can assume a planar configuration, analogous to that of PCDD/PCDF.

To estimate PCDD/PCDF releases in inventories, the Convention requires that the most advanced TEFs are used. These are, at present, the WHO-TEFs established by a WHO/IPCS expert meeting in 2005 (van den Berg *et al.* 2006) (see Annex 1). However, these have not yet been recognized or adopted by the Conference of the Parties. For the purpose of the Toolkit and its “order-of-magnitude” estimates of emission factors, the differences between the WHO-TEFs (either from 1998 or 2005) and the international TEFs (I-TEFs) previously established by the Committee on the Challenges of Modern Society of the North Atlantic Treaty Organization in 1988 are negligible. Therefore, the TEF-scheme accompanying the emission factors is not specified in the Toolkit. When reference is made to measured values, the TEF scheme used should be included.

## 1.5 Limitations

An inventory can provide valuable information on the magnitude of releases to each environmental medium and in products and residues. It can highlight sources for possible impacts but it cannot provide an accurate guide to the relative impact of these releases on human or ecosystem exposure since the fate of PCDD/PCDF varies considerably from one release source to another. The main purpose is to identify sources of unintentional POPs, prioritize them and undertake measures to prevent the formation and reduce or eliminate releases of unintentional POPs. Furthermore, measures taken to address PCDD/PCDF releases are equally suitable for other unintentional POPs.

The default emission factors presented in the Toolkit are best estimates derived from experimental results at well-documented sources (*i.e.*, taking into account technology, process characteristics and operating practices) or otherwise based on expert judgment. The results obtained for processes with similar characteristics are then aggregated into one emission factor representing “order of magnitude” release estimates, which do not describe accurately PCDD/PCDF releases from individual plants/facilities.

The default emission factors are assigned data quality ranks to enable an informed approach to estimating PCDD/PCDF releases. They should be applied with the specified level of confidence only when matching a specific situation in certain national circumstances. Annex 8 provides more information on data quality issues related to both emission factors and activity rates.

Most importantly, the Toolkit offers focused guidance on inventorying sources and releases of unintentional POPs. The Toolkit is based on systematic expert consultation, and can thus be considered as the most comprehensive and up-to-date compilation of emission factors for unintentional POPs.

## Chapter 2 Identifying Sources and Estimating Releases of PCDD/PCDF

The PCDD/PCDF inventory includes these five steps:

- Identify sources<sup>4</sup>;
- Select emission factors for the sources;
- Assign activity rates for each of the sources;
- Multiply the emission factor with the activity rate;
- Compile the inventory.

### 2.1 Identifying Sources

To assist Parties in identifying PCDD/PCDF sources at the national level, the Toolkit includes source categories as described in Annex C of the Stockholm Convention, Parts II and III. Since the list in Part III is indicative and open for additions, the Toolkit also contains further source categories that have been identified in existing inventories, national assessments, scientific studies, etc. In addition, it provides a simple screening process for identifying other sources not yet listed in the Toolkit.

#### Sources listed in the Toolkit

A country or region can begin identifying its PCDD/PCDF sources by determining the presence or absence within its borders of the PCDD/PCDF sources currently listed in the Toolkit. The Toolkit lists the source categories identified in Annex C as well as those identified by other means, such as national PCDD/PCDF inventories, scientific studies and reports.

The source categories listed in the Toolkit are divided into ten source groups. Table I.2.1 presents these ten source groups and the source categories currently listed in the Toolkit.

Table I.2.1 – Source Groups and Associated Source Categories						
Source Group	1. Waste Incineration		2. Ferrous and Non-Ferrous Metal Production	3. Heat and Power Generation	4. Production of Mineral Products	5. Transport
Source Categories	a	Municipal solid waste incineration	Iron ore sintering	Fossil fuel power plants	Cement production	4-Stroke engines
	b	Hazardous waste incineration	Coke production	Biomass power plants	Lime production	2-Stroke engines
	c	Medical waste incineration	Iron and steel production and foundries	Landfill, biogas combustion	Brick production	Diesel engines
	d	Light-fraction shredder waste incineration	Copper production	Household heating and cooking (biomass)	Glass production	Heavy oil fired engines
	e	Sewage sludge	Aluminum	Domestic heating	Ceramics production	

<sup>4</sup> A source that has been determined not to be present in the country is assigned the value “0” in the national inventory

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		incineration	production	(fossil fuels)		
	f	Waste wood and waste biomass incineration	Lead production		Asphalt mixing	
	g	Destruction of animal carcasses	Zinc production		Oil Shale Processing	
	h		Brass and bronze production			
	i		Magnesium production			
	j		Other non-ferrous metal production			
	k		Shredders			
	l		Thermal wire reclamation			
<b>Source Group</b>		<b>6. Open Burning Processes</b>	<b>7. Production and Use of Chemicals and Consumer Goods</b>	<b>8. Miscellaneous</b>	<b>9. Disposal and Landfill</b>	<b>10. Contaminated Sites and Hotspots</b>
<b>Source Categories</b>	a	Biomass burning	Pulp and paper production	Drying of biomass	Landfills, Waste Dumps and Landfill Mining	Sites used for the production of chlorine
	b	Waste burning and accidental fires	Chlorinated inorganic chemicals	Crematoria	Sewage and sewage treatment	Production sites of chlorinated organics and related deposits
	c		Chlorinated aliphatic chemicals	Smoke houses	Open water dumping	Application sites of PCDD/PCDF containing pesticides and chemicals
	d		Chlorinated aromatic chemicals	Dry cleaning	Composting	Timber manufacture and treatment sites
	e		Other chlorinated and non-chlorinated chemicals	Tobacco smoking	Waste oil treatment (non-thermal)	Textile and leather factories
	f		Petroleum refining			Use of PCB
	g		Textile production			Use of chlorine for production of metals and inorganic chemicals
	h		Leather refining			Waste incinerators
	i					Metal industries
	j					Fire Accidents
	K					Dredging of sediments; contaminated flood



						plains
	L					Other dumps/landfills of wastes from source groups 1-9
	m					Kaolin or ball clay sites

When an activity or process is identified but not described or not exactly matching the description provided in the Toolkit, the respective estimate of PCDD/PCDF releases can be included in the national inventory. The additional source will be inserted into the national inventory by adding extra lines into the respective source group (in the EXCEL spreadsheet). Such additions should be highlighted accordingly.<sup>5</sup>

### Sources not listed in the Toolkit

To identify PCDD/PCDF sources not currently listed in the Toolkit, it is necessary to determine whether chlorine (in elemental, organic or inorganic forms) is or was present in the processes or activities of interest. PCDD/PCDF formation is influenced by many factors. However, when chlorine is not present, PCDD/PCDF formation cannot occur; when chlorine is present, even as a trace element, PCDD/PCDF formation may occur.

When Parties have identified processes or activities that are potential PCDD/PCDF sources due to the presence or use of chlorine in some form, those potential sources should be thoroughly evaluated. Evaluations can begin by investigating existing inventories, the scientific literature, government reports, etc., to determine if the processes of interest or very similar processes have already been reported to release PCDD/PCDF. Additional guidance, including lists of processes and activities for which evidence of PCDD/PCDF formation and/or release exists but which are not addressed elsewhere in the Toolkit, is given in Annex 2.

## 2.2 Emission Factors

For each source category and/or source, it is necessary to obtain basic information about the design, operation, and other related factors that can substantially influence the magnitude of PCDD/PCDF releases. Based on this information, each source will be classified and placed in one of the several classes to which default emission factors are assigned.

Example questionnaires provided in Annex 3 may be useful in obtaining the information needed to classify source categories and so select appropriate emission factors. More specific suggestions on the information needed and potential avenues for obtaining such information for a source category may be found in Part II, in the chapters concerning source groups 1 through 10.

The default emission factors presented in the Toolkit are drawn from a variety of data sources, ranging from laboratory experiments, peer reviewed literature, dedicated experimental projects, to governmental or institutional reports. The emission factors for each class are best estimates based

<sup>5</sup> For example, if cremation of humans or animals is done in a way that neither reflects crematoria as described in category 8(b) for crematoria nor 1(g) for animal carcass incineration nor 6(b) for open burning of waste.

where possible on data measured at well-documented sources taking into account technology, process characteristics and operating practices, or otherwise estimates based on expert judgment. For the purpose of defining a default emission factor, results/processes with similar characteristics are aggregated into one emission factor. As such, the Toolkit's default emission factors are approximations intended to represent order of magnitude release estimates. They are suitable to derive national release inventories, set priorities, develop action plans and evaluate their efficacy; however, they should not be taken as accurately describing releases from individual plants/facilities.

The Toolkit methodology is designed so that both country-derived emission factors and the default emission factors presented in the Toolkit can be used. Default emission factors are recommended to be used for comparison or in cases where country-specific emission factors are not available.

### **2.3 Activity Rates**

Activity rates are values in unit per year of product manufactured ( *e.g.*, steel, sinter, cement, pulp, compost, *etc.*) or feed material processed ( *e.g.*, municipal waste, hazardous waste, coal, diesel fuel, bodies cremated, *etc.*), or annual quantities of material released ( *e.g.*, m<sup>3</sup> of flue gas, liters of wastewater, kilograms or tons of sludge generated, *etc.*).

Values for activity rates may be found in centralized statistical information assembled by state, provincial, national or international agencies, and they may be obtained from trade associations and owner/operators of facilities. Potential sources of information on activity rates include the following:

- National statistics;
- National energy balance;
- Regional economic activity records including national production and import/export data;
- International statistics such as EUROSTAT, OECD, FAO, World Bank *etc.*
- Local operating and permitting records of industrial facilities;
- Industry association data;
- Historical production and industry data;
- Other release inventories such as the inventory of criteria pollutants and or greenhouse gases;
- Questionnaires;
- Pollution Release and Transfer Registers (PRTs).

When the activity rate for an industrial source category is not available but the nameplate capacity is known, an activity rate can be estimated by multiplying capacity by the domestic capacity utilization factor (CUF). If no domestic CUF is available, a regional or global CUF may be used and, if neither regional nor global CUF is available, the Toolkit Expert Group may provide an appropriate value.

Activity rates for diffuse source categories, such as traffic, open burning of domestic waste, agricultural residues, *etc.*, are best characterized by drawing from centrally available data.

## 2.4 Release Estimates

Once PCDD/PCDF sources are identified and classified, emission factors selected and national or regional activity rates determined, the estimation of the total annual releases by source group, source category and class is relatively simple and straightforward.

For a source class, PCDD/PCDF releases per year are calculated according to the equation below. The activity rate is multiplied by each of the five emission factors and the sum of the five resulting values represents the quantity of PCDD/PCDF released annually from the source class.

$$\begin{aligned} \text{PCDD/PCDF released, grams TEQ/year} = & \text{Activity Rate} \times \text{Emission Factor}_{\text{Air}} \\ & + \text{Activity Rate} \times \text{Emission Factor}_{\text{Water}} \\ & + \text{Activity Rate} \times \text{Emission Factor}_{\text{Land}} \\ & + \text{Activity Rate} \times \text{Emission Factor}_{\text{Product}} \\ & + \text{Activity Rate} \times \text{Emission Factor}_{\text{Residue}} \end{aligned}$$

For a source category, the annual PCDD/PCDF release is calculated as the sum of the total annual releases for each class within the category.

For each source group, the annual PCDD/PCDF release is the sum of the annual releases calculated for each source category in the source group.

For a country or region, the total annual PCDD/PCDF release is the sum of the annual releases from all source groups.

The spreadsheet will be used to determine annual releases according to source groups and the year of reporting.

## 2.5 Compilation of PCDD/PCDF Inventory

The Toolkit simplifies and expedites the calculations described above by providing an Excel spreadsheet that includes a list of the source categories addressed in the Toolkit, along with their associated classes and accompanying default emission factors. Once the activity rates for all classes within the source categories that have been determined to be present within a country or region are entered into the spreadsheet, annual PCDD/PCDF releases are automatically calculated for each source category. A summarizing worksheet provides an overview of all releases according to vectors (air, water, land, product, residue) and source groups.

Newly identified sources can also be included in the spreadsheet, along with their associated emission factors and activity rates. Their releases are also automatically calculated and included in the final results. If desired, a country can replace the Toolkit's default emission factors with their own emission factors that have been otherwise derived.

These and other issues related to the preparation of inventories and reporting of releases are discussed in greater detail in Chapter 3 Reporting of Releases.

## Chapter 3 Reporting of Releases

### 3.1 Categorization of Sources

Source categories of unintentional POPs releases under the Stockholm Convention are listed in Annex C Part II and Part III to the Convention. These source categories are also among those considered in the Toolkit, where they are placed into ten source groups to facilitate the development of national release inventories and reporting of POPs releases.

The standard format to report PCDD/PCDF releases through national reports under Article 15 is included in Annex 5, Table III.5.1.

Some countries also report POPs releases to air and a number of other pollutants under the UNECE Convention on Long-Range Transboundary Air Pollution (CLRTAP). For these countries, a brief explanation of source categorization under CLRTAP, including a list of source categories under the Stockholm Convention and their equivalent designations under CLRTAP, is presented in Annex 5, Table III.5.2.

Parties are encouraged to report releases of unintentional POPs in national reports submitted pursuant to Article 15 of the Convention, according to the source categories listed in Annex C of the Convention, grouped into the source groups specified in the Toolkit. By complying with this approach, Parties will ensure that the following conditions are met:

- Estimates of unintentional POPs releases are readily comparable;
- Regional and global release summaries can be easily prepared; and
- Time trends can be readily elaborated for the purpose of effectiveness evaluation under Article 16 of the Convention.

### 3.2 Baseline Release Estimates, Updating, Revisions, and Projections

Article 5, paragraph (a) (i) of the Stockholm Convention requires that Parties evaluate current and projected releases, including the development and maintenance of source inventories and release estimates of chemicals listed in Annex C, Part I, taking into consideration the source categories identified in Annex C, Part II and III, of the Convention.

In practice, this means that Parties must prepare their initial release estimates and update these estimates at regular intervals (*e.g.* every five years). Parties may also find it necessary to revise their initial and subsequent estimates in order to establish and maintain the consistency necessary for discerning meaningful trends in releases over time.

The **baseline release estimate** is the first inventory of sources and releases of Annex C POPs elaborated by a Party, usually as part of the National Implementation Plan developed under Article 7. This first inventory serves as a baseline against which subsequent updated release estimates are assessed in order to establish trends in releases over time and evaluate the efficacy of the adopted strategies for minimizing and/or eliminating PCDD/PCDF and other unintentional POPs releases.

As schematized in Figure I.3.1, **updating of the inventory begins** with an examination of the previous/baseline inventory to identify the approach used, including:

- The classification of sources and emission factors used
- Information sources based on which activity rates were estimated
- Assumptions and expert judgment applied to fill the gaps

**In a second step**, the developer of the inventory should **review changes in data since the baseline inventory**, in particular by checking for factors that may influence changes in releases over time. These include: economic and/or demographic growth, changes in technologies in particular through phasing in BAT and BEP, building, reconstruction or close down of production facilities, substitution of fuels, introduction of abatement techniques, identification of new sources, and others.

It is also important to **check whether new or revised emission factors have become available or new source categories or classes have been included in the Toolkit**. Once these data and information are collected, the developer of the inventory will proceed with the reclassification of sources to reflect the current situation in the particular reference year and with the establishment of activity rates for the reference year.

Once the information is assessed and the inventory is updated to reflect economic, demographic and technical changes, the **need to revise the previous inventories**, including the baseline, may arise. Revising previous inventories so that new or revised emission factors and new source categories and classes are incorporated is especially important.

Besides such changes in the Toolkit methodology, some **specific national factors may also trigger the need for revision**. These are usually related to the availability at the country level of **new or corrected information/knowledge**, *e.g.* correction of past activity estimates or the discovery of sources that existed in the past but were not considered in previous inventories due to lack of adequate information at that time.

**The revision of the previous inventories aims to correct the estimates therein, by including missing information, filling gaps, using the same set of emission factors, applying the same assumptions, expert judgment as in the updated inventory.**

Only after this stage, the developer of the inventory will be able to calculate updated releases **and establish consistent trends in releases over time**. If sources are reclassified and/or emission factors have been revised, new factors must be assigned accordingly; if the source classification has not changed, nor the emission factors, the same factors are applied; releases are finally estimated by multiplying the emission factors with the corresponding activity rates.

**Maintaining all these stages in the inventory updating and revision process is essential to ensure that coherent trends over time can be computed based on comparable and consistent results over time.**

The same approach needs to be applied consistently in all release estimates to ensure consistency of results over time and to enable the assessment of trends over time.

If the approach changes over time, if new or corrected information or knowledge becomes available at the country level, **previous inventories need to be revised accordingly and one single approach used for all inventories**. Otherwise it would not be possible to compare data from the different reference years and establish consistent trends over time.

**Projections of future release estimates** may be elaborated by Parties using the same methodology, by considering:

- Appropriate emission factors based on planned or expected changes in technologies, raw materials, fuels, abatement techniques or other key parameters which could influence release estimates (*e.g.* triggered by the action plan developed under Article 5 of the Convention).
- Projections of future activity rates for certain source categories based on *e.g.* - expected socio-economic development, production plans for a particular source category or source group, etc.

The example inventory 1 shows an illustration of the inventories' update and revision process.

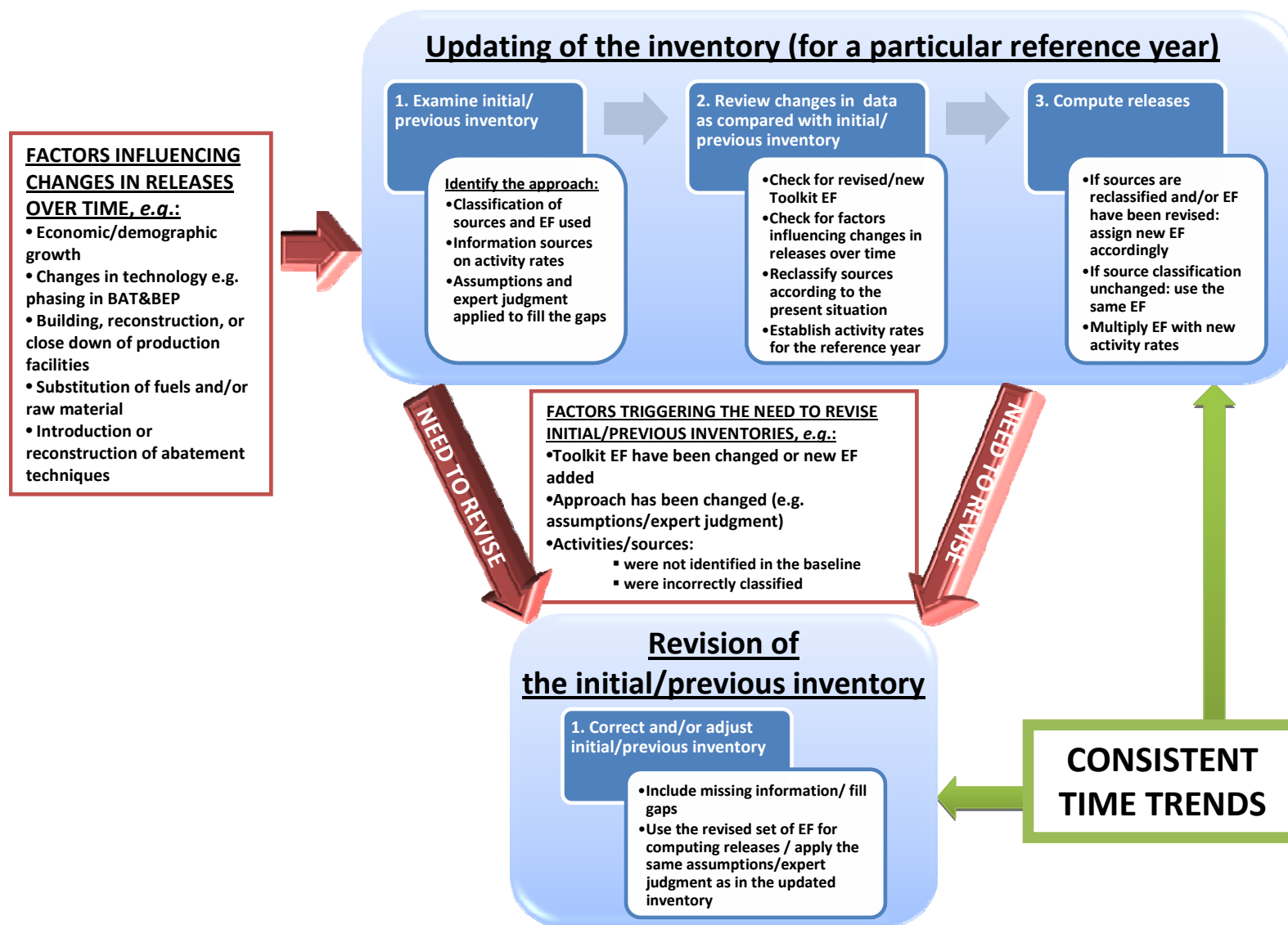


Figure I.3.1 Establishing trends in POPs releases over time

## Chapter 4 Data Quality

Source inventories and release estimates reported under Article 15 should be:

- Reliable,
- Consistent over time,
- Comparable between countries,
- Transparent, and
- Complete.

**Reliable** inventories entail coherent application of internationally acknowledged methodologies such as the Toolkit and the use of best available national information.

To achieve **consistency** over time, the same approach should be used over time to establish consistent time trends. To ensure **comparability between countries**, all countries should report according to the same source groups and source categorization.

For **transparent** estimates, the approach, methodology, information, and assumptions used should be clearly described, documented and archived to facilitate inventory updates in the future.

For **complete** release inventories, all relevant source categories, all sources within those categories and all relevant release vectors have to be considered in the whole country. The inventory should also include information on source categories that do not exist or are not operational in the country during the reference year.

### 4.1 Quality Assurance and Quality Control (QA/QC)

The following quality assurance and quality control measures (QA/QC) should be applied to ensure that the source inventory and release estimates meet the quality criteria described above:

#### Activity Rates

- Align the unit of the activity rate with the unit of the emission factor.
- Pay attention to orders of magnitude while recalculating the activity rates and applying the emission factors.
- Explain clearly and completely all assumptions made in filling gaps in activity rates (see also “completeness”).
- Explain clearly and completely the process of classification of sources and the way activity rates were derived.

#### Emission Factors

- The Toolkit expert group is mandated to evaluate all emission factors that are or will be included in the Toolkit to determine that they are scientifically sound.
- National emission factors should only be derived from measured data of adequate quality *e.g.* the application of standard sampling and analytical methods; proven laboratory experience and good documentation are pre-requisites of high quality data.



- The classification of sources and choice of emission factors have to be explained, documented and archived.
- Consideration has to be given to units and orders of magnitude.

### Completeness of Data

- Whenever practical and appropriate, individual plant questionnaires may be used to gather information for large point sources<sup>6</sup>.
- Questionnaires provide useful information for the classification of plants and selection of emission factors. Since the return rate of the questionnaires is likely to be low, incomplete information-data gaps- will need to be covered by making assumptions about certain sources, where no specific information can be collected. Approaches will vary, but all assumptions should be clearly described in order to facilitate inventory updates in the following years or revisions in light of improved information.
- To determine complete activity rates, a combination of questionnaires (for large point sources) and national statistics should be used.
- When reporting the inventory results, it should be distinguished between “not applicable” *e.g.* the source category does not exist or is not operational in the country, and “not estimated” *e.g.* the source category is relevant but there was no sufficient information to estimate the releases.

### Additional Considerations for Assessment of Inventory Results

- Compare national inventory results with results from other countries (see Annex 7).
- Compare national inventory results across different time periods: differences have to be justified, documented and logically explainable.

## 4.2 Data quality

Possibilities of indicating the confidence in the data used to generate emissions estimates may be as follows:

- Reporting of ranges (gives a good indication of confidence in data, however it may create problems while summarizing releases from more countries, therefore suitable only for reporting at the national level);
- Simple qualifiers, *i.e.*, data quality codes “high”, “medium”, “low” as outlined in Annex 8.

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<sup>6</sup> Large point sources include major industrial emitters, and the collection of information on their activity rates should be given priority. Definition of the large point sources as described for different industrial sectors in Annex 1 of the Directive 2008/1/EC on Integrated Pollution Prevention and Control (IPPC) may be used for orientation. As an example, emission from the following large point sources are regulated by the IPPC directive:

- combustion installations with a rated thermal input exceeding 50 MW;
- installations for the production of iron or steel with a capacity exceeding 2,5 tons per hour;
- installations for the production of cement with a capacity exceeding 500 tons per day, etc.

More details can be found at <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32008L0001:EN:NOT>

Qualifiers may be applied to both emission factors and activity data to discern the overall confidence in the inventory's results. Quality ranks are assigned to default emission factors by the Toolkit expert group to enable informed use of the methodology to assess PCDD/PCDF releases. Technical annexes provide complementary information on how default emission factors were derived to ensure that they are applied with the specified level of confidence only when matching a specific situation. Furthermore, guidance on assessing data quality criteria for calculating activity rates is provided in Annex 8.

More details on data quality and inventory QA/QC can be found in Part II Default Emission Factors.

## **PART II    DEFAULT EMISSION FACTORS**

Part II contains a compilation of PCDD/PCDF emission factors for all source categories listed in Annex C Part II and III of the Stockholm Convention. Emission factors for certain other unintentional POPs sources are presented in Part III of the Toolkit. The source categories are grouped into 10 source groups. Neither the sequence of the groups, nor the sequence of the source categories within the groups implies any ranking of the importance of each group within a country's unintentional POPs inventory.

The chapters on default emission factors begin with a brief description of the source group's characteristics followed by an overview of relevant source categories, including major unintentional POPs release routes. Reference is made to the Stockholm Convention and information on each source category's relevance to Article 5, Annex C is provided. A series of example inventories have also been compiled to provide specific examples of inventories of sources and releases of unintentional POPs. The example inventories were developed to illustrate the inventory process for each of the ten source groups covered by the Toolkit.

Emission factors are provided for five release vectors, *i.e.*, air, water, land, product, residue.

Individual source categories included in one source group are addressed by the following sub-chapters:

- Brief description of the source category and potential unintentional POPs releases, linked to the BAT&BEP Guidelines where appropriate;
- PCDD/PCDF emission factors for the particular classes along with detailed information needed for the classification of the sources and selection of most appropriate emission factors;
- If available, emission factors for other unintentional POPs are provided in Annexes;
- Useful guidance facilitating the assessment of relevant activity rates;
- Assessment of the level of confidence associated with emission factors by assigning data quality rating;
- Detailed information on how the emission factors were derived is also provided in Annexes, along with an overview of all recent revisions performed by the Toolkit expert group; and
- Example inventories for every source group are included in Part III.

## 1 – Waste Incineration

Waste incinerators (including co-incinerators of municipal, hazardous or medical waste or of sewage sludge) are recognized in Annex C, Part II, of the Stockholm Convention as having the potential for comparatively high formation and release of PCDD/PCDF. For the purposes of identifying sources of PCDD/PCDF and estimating their releases, the Toolkit defines source categories of waste incinerators according to the type of waste incinerated, as indicated in Table II.1.1.

**Table II.1.1 Overview of source categories included in group 1 - Waste Incineration**

1 - Waste incineration		Potential release route				
Source categories		Air	Water	Land	Product	Residue
a	Municipal solid waste incineration	X	(x)			X
b	Hazardous waste incineration	X	(x)			X
c	Medical waste incineration	X	(x)			X
d	Light-fraction shredder waste incineration	X				X
e	Sewage sludge incineration	X	(x)			X
f	Waste wood and waste biomass incineration	X				X
g	Destruction of animal carcasses	X				X

**Table II.1.2 Relevance to Article 5, Annex C of the Stockholm Convention**

No	Toolkit source category	Part II	Part III	Relevant source category in Annex C
1a	Municipal solid waste incineration	X		Waste incinerators
1b	Hazardous waste incineration	X		Waste incinerators
1c	Medical waste incineration	X		Waste incinerators
1d	Light-fraction shredder waste incineration	X		Waste incinerators
1e	Sewage sludge incineration	X		Waste incinerators
1f	Waste wood and waste biomass incineration	X		Waste incinerators
1g	Destruction of animal carcasses		X	Destruction of animal carcasses

Each source category may represent many individual waste incinerators, with each being relatively unique in design, construction and operation. Moreover, while specific wastes may share a common description, they may differ in composition and combustion characteristics. For example, the composition and combustion characteristics of municipal waste are known to vary greatly from city to city, country to country and even season to season.

An example of elaborating a source inventory and release estimate for this source group is included in the example inventory 2.

### 1a Municipal Solid Waste Incinerators

Municipal solid waste (MSW) is defined differently among countries as well as among international agreements. MSW typically includes almost any solid waste generated by households during normal daily life and it also commonly includes wastes produced in industrial, commercial and

agricultural activities. Common constituents in MSW include paper and cardboard, plastics, food and kitchen residues, cloth and leather, wood, glass, and metals as well as dirt and rocks and other inert materials. Small quantities of hazardous materials such as batteries, paints, drugs, and some household chemicals also occur in MSW. Nonetheless, most authorities consider MSW as non-hazardous.

MSW incinerators range from batch-fed muffle furnaces to highly sophisticated mass burn systems with grates, heat recovery boilers, and complex air pollution control (APC) systems. In capacity, they range from a few tons per day in small, batch-fed units to more than two thousand tons per day in massive, continuously-fed facilities. A thorough, detailed discussion of more advanced MSW incinerators is given in the BAT&BEP Guidelines.

MSW incinerators release PCDD/PCDF in flue gas, fly ash,<sup>7</sup> bottom ash<sup>8</sup>, wastewater and filter cake from wastewater treatment. For the most advanced incinerators, PCDD/PCDF concentrations per unit mass of these outputs can be ranked as follows: filter cake > fly ash >> bottom ash >> wastewater > flue gas.

### Emission Factors

PCDD/PCDF emission factors for the four classes of MSW incinerators are listed in Table II.1.3. Detailed information on the derivation of these emission factors can be found in Annex 9.

### Guidance for Classification of Sources

For the purpose of selecting emission factors, four broadly defined classes of MSW incinerators are as follows:

**Class 1** includes MSW incinerators that are simple, batch-fed furnaces with no APC systems and capacities of 500 kg/h or less.

**Class 2** includes MSW incinerators that are continuously fed, controlled combustors equipped with minimal APC systems, such as electrostatic precipitators, multi-cyclones and/or simple scrubbers.

**Class 3** includes MSW incinerators that are continuously fed, controlled combustors equipped with improved APC systems such as a combination of electrostatic precipitators and multiple scrubbers, a combination of spray-dryers and baghouse, or similar combinations.

**Class 4** is limited to state-of-the-art MSW incinerators equipped with sophisticated APC technologies, such as activated carbon adsorption units or SCR DeDiox<sup>®</sup> systems that should be capable of ensuring compliance with a strictly enforced regulatory value for air emissions in flue gases that is equivalent to 0.1 ng TEQ/Nm<sup>3</sup> at 11% O<sub>2</sub>).

**Table II.1.3 PCDD/PCDF emission factors for source category 1a Municipal Solid Waste Incinerators**

1a	Municipal Solid Waste Incinerators	Emission Factors (µg TEQ/t MSW incinerated)	
Classification		Air	Residue
			Fly Ash

<sup>7</sup> The term “fly ash” is used here to include dust from boiler and dedusting, residues from flue gas cleaning without filter dust, residues from flue gas cleaning and filter dust.

<sup>8</sup> The term “bottom ash” is used here also to include slag.

1	Low technology combustion, no APCS	3,500	ND	75
2	Controlled combustion with minimal APCS	350	500	15
3	Controlled combustion with good APCS	30	200	7
4	High technology combustion, sophisticated APCS	0.5	15	1.5

In addition, PCB emission factors to air have been determined in a measurement campaign in France (Delepine *et al.* 2011). These are mentioned in Annex 9.

### Activity rates

Activity rates for MSW incineration may be obtained from various sources, such as the following:

- State, provincial, national and/or international agencies that gather centralized statistical information, including MSW generation and treatment;
- State, provincial and national agencies that issue permits to MSW incinerators;
- Owner/operators of MSW incineration facilities (by questionnaires);
- Other release inventories such as the inventory of mercury sources and releases, criteria pollutants and/or greenhouse gases;
- Associations of MSW owner/operators;
- Waste recycling organizations;
- International statistics such as EUROSTAT, OECD, World Bank, etc.;

### Level of Confidence

Based on the relatively comprehensive data coverage and the level of agreement among the different datasets, the emission factors are assigned a medium confidence level.

## 1b Hazardous Waste Incinerators

Hazardous waste (HW) refers to residues and wastes that are classified as hazardous due to their characteristics or that contain materials regarded as hazardous. For example, hazardous wastes are commonly generated during the manufacture of chemicals, including commercial chemicals, pharmaceuticals, pesticides, etc. In general, all materials that require special precautions and restrictions during handling and use and any consumer goods that are labeled as hazardous and have entered the waste stream are considered hazardous waste. These include solvents and other volatile hydrocarbons, paints and dyes, chemicals including pesticides and other halogenated chemicals, pharmaceutical products, batteries, fuels, oils and other lubricants, as well as goods containing heavy metals. Also, all materials contaminated with these materials such as soaked rags or paper, treated wood, production residues, etc., must be considered hazardous waste.

The term “hazardous waste” as used in the Toolkit does not include medical waste since hazardous and medical wastes have different origins and the technologies for their treatment are different (see source category 1c Medical Waste Incinerators). Typically HW incinerators are special technology incinerators or rotary kiln type furnaces. Special technology incinerators include very low technology grate, or muffle furnaces. Since the classification of hazardous waste is highly dependent on country-specific legislation and on the number of different technologies used for hazardous waste,

incineration plants can have many features. A detailed discussion of hazardous waste incineration technologies can be found in the BAT&BEP Guidelines.

Co-combustion in cement kilns is addressed in Group 4 – Mineral Products.

### Emission Factors

PCDD/PCDF emission factors for four classes of HW incinerators are listed in Table II.1.4. Detailed information on the derivation of these emission factors can be found in Annex 10.

### Guidance for Classification of Sources

For the purpose of selecting emission factors, four broadly defined classes of HW incinerators are defined as follows:

**Class 1** includes very small (< 500 kg/h) and simple furnaces operated in a batch-fed mode without any APC system for stack gases, e.g., muffle ovens, with flue gas volume flow rate of about 17,500 Nm<sup>3</sup>/t of hazardous waste

**Class 2** includes HW incinerators with controlled combustion and minimal APC systems, with flue gas volume flow rate to 15,000 Nm<sup>3</sup>/t of hazardous waste.

**Class 3** incinerators have further improved combustion efficiencies and more efficient systems resulting in PCDD/PCDF concentrations of about 1 ng TEQ/Nm<sup>3</sup> (at 11% O<sub>2</sub>). Also, the specific flue gas volume flow rate is reduced to 10,000 Nm<sup>3</sup>/t HW.

**Class 4** is limited to highly sophisticated hazardous waste incineration plants that are capable of complying with a regulatory value of 0.1 ng TEQ/Nm<sup>3</sup> (at 11% O<sub>2</sub>), such as legislated in the in European Union. Class 4 represents the current state-of-the-art in HW incineration and APC technology with stack gas flow rates of some 7,500 Nm<sup>3</sup>/t HW.

**Table II.1.4 PCDD/PCDF emission factors for source category 1b Hazardous Waste Incinerators**

1b	Hazardous Waste Incinerators	Emission Factors (µg TEQ/t HW burned)	
		Air	Residue (fly ash only)
1	Low technology combustion, no APCS	35,000	9,000
2	Controlled combustion with minimal APCS	350	900
3	Controlled combustion with good APCS	10	450
4	High technology combustion, sophisticated APCS	0.75	30

PCB emission factors to air have been derived in a measurement campaign in France (Delepine *et al.* 2011). These are mentioned in Annex 10.

### Activity rates

Activity rates for HW incineration may be obtained from various sources, such as the following:

- State, provincial, national and/or international agencies that gather centralized statistical information, including hazardous waste generation and treatment;
- State, provincial and national agencies that issue permits to HW incinerators;
- Owner/operators of HW incineration facilities (by questionnaires);

- Other release inventories such as the inventory of mercury sources and releases, criteria pollutants and/or greenhouse gases;
- Associations of HW owner/operators
- International statistics such as EUROSTAT, OECD, World Bank, etc.;

### **Level of Confidence**

The default emission factors are based on a certain number of assumptions detailed in Annex 10. In addition, data are lacking for bottom ash concentrations. The emission factors are thus assigned a low confidence level.

## **1c Medical Waste Incinerators**

Medical waste (MW) is considered to be every waste generated from medical activities regardless if these activities take place in a hospital or are performed by a medical doctor, dentist or any other healthcare facility or provider. In many cases, waste generated during these activities contains infectious materials, human secretions, blood, pharmaceuticals and packaging materials and/or tools used during or for the medical treatment of people or animals. To destroy viruses, bacteria, and pathogens this waste is often thermally treated (by incineration or pyrolysis). Further, due to its origin and its composition, medical waste can contain toxic chemicals, *e.g.*, heavy metals or precursors, high concentrations of organic (polyvinyl chloride and certain pharmaceuticals) and inorganic (saline solution and body fluids) chlorine that may alter combustion characteristics, and absent proper technology may enhance PCDD/PCDF formation.

MW is a waste that requires special surveillance and incineration of all wastes generated within a hospital has been regarded as an efficient way to dispose of these wastes. However, it has also been shown that incineration of medical waste in small and poorly controlled incinerators is a major source of PCDD/PCDF.

Typically, medical waste is incinerated locally at the hospital or any other medical facility in small furnaces in a batch-type mode. In many cases, larger and centralized medical waste incineration facilities are operated only for eight hours a day and five days a week. Large and continuously operated medical waste incinerators are rare and mostly found in developed regions and countries. Also, waste heat recovery boilers are rare. For a more detailed discussion of medical waste incinerators refer to the BAT&BEP Guidelines.

### **Emission Factors**

PCDD/PCDF emission factors for four classes of MW incinerators are listed in Table II.1.5. Detailed information on how these emission factors have been derived can be found in Annex 11.

### **Guidance for Classification of Sources**

For selection of the most appropriate emission factors, the range of MW incineration technologies is divided into four classes:

**Class 1** includes very small and simple, small box type incinerators operated intermittently (in which waste loads are ignited and left) with no secondary combustion chamber, no temperature controls and no air pollution control equipment.



**Class 2** applies to all medical waste incinerators with controlled combustion and an afterburner, but still operated in a batch type mode.

**Class 3** includes controlled batch-type plants, with good APC systems in place, e.g., ESPs or preferably baghouse filters.

**Class 4** includes highly sophisticated medical waste incineration plants that are capable of complying with an air emission 0.1 ng TEQ/Nm<sup>3</sup> (at 11% O<sub>2</sub>). Whether these plants are continuous or batch type operations is not relevant when they are preheated with oil or natural gas to achieve a furnace operating temperature of usually well above 900°C or higher before medical waste is introduced into the furnace.

**Table II.1.5 PCDD/PCDF emission factors for source category 1c Medical Waste Incinerators**

1c	Medical Waste Incinerators	Emission Factors (µg TEQ/t MW incinerated)	
		Air	Residue
1	Uncontrolled batch type combustion, no APCS	40,000	200*
2	Controlled, batch type combustion, no or minimal APCS	3,000	20*
3	Controlled, batch type combustion, good APCS	525	920**
4	High technology, continuous, controlled combustion, sophisticated APCS	1	150**

\* Refers only to bottom ash left in the combustion chamber

\*\* Refers to combined bottom and fly ashes.

### Activity rates

Activity rates for MW incineration may be obtained from various sources, such as the following:

- Ministry of health;
- State, provincial, national and/or international agencies that gather centralized statistical information, including medical waste generation and treatment;
- State, provincial and national agencies that issue permits to MW incinerators;
- Hospitals and other healthcare facilities with on-site MW incinerators (by questionnaires);
- Owner/operators of commercial MW incineration facilities (by questionnaires);
- Other release inventories such as the inventory of mercury sources and releases, criteria pollutants and/or greenhouse gases;
- Associations of MW incinerator owner/operators
- International statistics such as EUROSTAT, OECD, World Bank, etc.;

### Level of Confidence

For well controlled processes such as those described in class 3 and 4, emission factors are assigned a medium confidence level. For class 2, results for bottom ash from a medical waste incinerator in Thailand were extremely high, showing a large variation from the levels calculated using the corresponding emission factor. For class 1 and 2, where the processes are less controlled, emission factors are thus assigned a low confidence level.

## 1d Light-Fraction Shredder Waste Incinerators

Light-fraction shredder waste (LFSW) (also sometimes referred to as shredder “fluff” or light weight aggregate) describes the light fraction derived from shredding large items such as end-of-life vehicles, white goods, bulky containers, etc. that are shredded in order to reduce the volume as well as enable the separation of recoverable materials such as metals. Typical separation mechanisms include screening, sifting, and fractionation processes, in which weight differences between the materials or the magnetic properties of ferrous metals allow the shredder aggregate to be fractionated into ferrous metals, non-ferrous metals, glass, other heavy inerts, and light-weight fractions. In some cases the light fraction has little use and may be combusted for disposal.

### Emission Factors

PCDD/PCDF emission factors for three classes of LFSW incinerators are listed in Table II.1.6. Detailed information on how these emission factors have been derived can be found in Annex 12.

### Guidance for Classification of Sources

For selection of the most appropriate emission factors, the range of LFSW incineration technologies is divided into three classes:

**Class 1** includes very simple stationary grate furnaces with no combustion controls and no APC equipment. Batch type furnaces without any APC also fall into class 1.

**Class 2** includes all other furnaces with some kind of combustion control technology such as under and/or over fire air, stoker controls, fluidized beds, etc. including the facilities with some kind of APC system such as an ESP, baghouse or wet scrubber for dust removal. Class 2 also applies to LFSW incinerators with controlled combustion and adequate APC equipment, which, however, are still operated in a batch type mode.

**Class 3** includes highly sophisticated incineration plants that are capable of achieving a regulatory value for air emissions equivalent to 0.1 ng TEQ/Nm<sup>3</sup> (at 11% O<sub>2</sub>).

**Table II.1.6 PCDD/PCDF emission factors for source category 1d Light-Fraction Shredder Waste Incinerators**

1d	Light-Fraction Shredder Waste Incinerators	Emission Factors (µg TEQ/t LFSW incinerated)	
		Air	Residue
Classification			
1	Uncontrolled batch type combustion, no APCS	1,000	ND
2	Controlled, batch type combustion, no or minimal APCS	50	ND
3	High technology, continuous, controlled combustion, sophisticated APCS	1	150

### Activity rates

Activity rates for LFSW incineration are most likely to be available from sources such as the following:  
following:

- State, provincial, national and/or international agencies that gather centralized statistical information, including waste generation and treatment;
- State, provincial and national agencies that issue permits to LFSW incinerators;

- Owner/operators of LFSW incineration facilities (by questionnaires);
- Associations of LFSW owner/operators;
- Waste recycling organizations
- Other release inventories such as the inventory of mercury, criteria pollutants and/or greenhouse gases;
- International statistics such as EUROSTAT, OECD, World Bank, etc.;

### **Level of Confidence**

Based on the geographical coverage of emission data used for deriving emission factors for this category, class 2 and 3 emission factors are assigned a medium level of confidence. No accurate data are available for class 1, in which case the emission factor is assigned a low confidence level.

## **1e Sewage Sludge Incinerators**

Sewage sludge is produced from all wastewater treatment processes regardless of the wastewater's origin (e.g., wastewater from municipal, agricultural or industrial activities). When untreated, such wastewater always contains solids, which are normally removed as sludge during the treatment process. Since PCDD/PCDF are almost insoluble in water, the majority of the PCDD/PCDF adsorb to the solids present in the wastewater. These solids along with the adsorbed PCDD/PCDF can be removed by filtration or flocculation, so that the PCDD/PCDF are collected in the wastewater treatment sludge. This sludge can be disposed of in a variety of ways, including combustion in dedicated incinerators. A detailed discussion of sewage sludge incineration technologies is presented in the BAT&BEP Guidelines.

Disposal of sewage sludge in landfills is addressed in Group 9 – Disposal and Landfill; combustion with energy recovery, in Group 7 – Production and Use of Chemicals and Consumer Goods; co-combustion in boilers and fossil fuel power plants, in Group 3 – Power Generation and Heating; and co-combustion in cement kilns, in Group 4 – Mineral Products.

### **Emission Factors**

PCDD/PCDF emission factors for three classes of sewage sludge incinerators are listed in Table II.1.7. Detailed information on the derivation of these emission factors can be found in Annex 13.

### **Guidance for Classification of Sources**

For selection of the most appropriate emission factors, the range of sewage sludge incineration technologies is divided into three classes:

**Class 1** includes older furnaces with batch type operation and no or minimal APC system. Incinerators in this class have a flue gas volume flow rate of about 12,500 Nm<sup>3</sup>/t of sewage sludge burned

**Class 2** includes updated, controlled combustion, continuous-feed incinerators equipped with APC systems.

**Class 3** includes modern state-of-the-art facilities, continuous-feed fluidized bed incinerators with optimized APC systems capable of consistently meeting the emission limits equivalent to 0.1 ng TEQ/Nm<sup>3</sup> (at 11% O<sub>2</sub>)

### **Table II.1.7 PCDD/PCDF emission factors for source category 1e Sewage Sludge Incinerators**

1e	Sewage Sludge Incinerators	Emission Factors ( $\mu\text{g TEQ/t}$ of sewage sludge)	
		Air	Residue
1	Older furnaces, batch type operation, no or very little APCS	50	23
2	Updated, continuously operated and controlled facilities, some APCS	4	0.5
3	Modern state-of-the-art facilities, continuous, controlled operation, full APCS	0.4	0.5

PCB emission factors to air have been derived in a measurement campaign in France (Delepine *et al.* 2011). These are presented in Annex 13.

### Activity rates

Activity rates for sewage sludge incineration may be available from:

- State, provincial, national and/or international agencies that gather centralized statistical information, including sewage sludge generation and treatment;
- State, provincial and national agencies that issue permits to sewage sludge incinerators;
- Owner/operators of sewage sludge incineration facilities (by questionnaires);
- Sewage sludge (biosolids) recycling organizations;
- Other release inventories such as the inventory of mercury, criteria pollutants and/or greenhouse gases;
- Pollution Release and Transport Registers (PRTR).
- International statistics such as EUROSTAT, OECD, World Bank etc.

### Level of Confidence

Based on the consistency among the data sets used to derive the emission factors, these are provided with medium confidence.

## 1f Waste Wood and Waste Biomass Incinerators

Contaminated wood and other contaminated biomass can result from many anthropogenic activities, especially wood processing industries (*e.g.*, building materials, furniture, packing materials, toys, ship building, general construction, etc.) as well as construction and demolition debris. Such wood/biomass waste may contain paints, coatings, pesticides, preservatives, anti-fouling agents, and many other potentially problematic materials. These materials, when incinerated together with the biomass, can enhance the formation of PCDD/PCDF during combustion.

Biomass with a high content of chlorine (organic or inorganic) or heavy metals such as copper, lead, tin, or cadmium typically result in higher PCDD/PCDF emissions than the burning of virgin biomass. Combustion of clean biomass for generation of steam/heat is addressed in Group 3 –Power Generation and Heating, and open burning of either “clean” biomass or contaminated biomass is addressed in Group 6 – Open Burning Processes.

## Emission Factors

PCDD/PCDF emission factors for three classes of waste wood and waste biomass incinerators are listed in Table II.1.8. Detailed information on the derivation of these emission factors can be found in Annex 14.

### Guidance for Classification of Sources

For selection of the most appropriate emission factors, the range of waste wood and waste biomass incineration technologies is divided into three classes:

**Class 1** includes older, batch-fed furnaces with no APC system.

**Class 2** includes updated, controlled, continuously-fed facilities that are equipped with some APC system.

**Class 3** includes modern, continuously-fed and controlled, state-of-the-art facilities, equipped with full APC systems capable of meeting emission limits equivalent to 0.1 ng TEQ/Nm<sup>3</sup> (at 11% O<sub>2</sub>).

**Table II.1.8 PCDD/PCDF emission factors for source category 1f Waste Wood and Waste Biomass Incinerators**

1f	Waste Wood and Waste Biomass Incinerators	Emission Factors (µg TEQ/t biomass burned)	
		Air	Residue (fly ash only)
1	Older furnaces, batch type operation, no APCS	100	1,000
2	Updated, continuously operated and controlled facilities, some APCS	10	10
3	Modern state-of-the-art facilities, continuous controlled operation, full APCS	1	0.2

### Activity rates

Activity rates for waste wood/biomass incineration may be available from

- State, provincial, national and/or international agencies that gather centralized statistical information;
- National energy balance;
- State, provincial and national agencies that issue permits to waste wood/biomass incinerators;
- Owner/operators of waste wood/biomass incineration facilities (by questionnaires);
- Other release inventories such as the inventory of mercury, criteria pollutants and/or greenhouse gases;
- Pollution Release and Transport Registers (PRTR).
- International statistics such as EUROSTAT, OECD, World Bank etc.

### Level of Confidence

The default emission factors for all three classes were determined based on reported concentrations from a number of studies in Europe and North America. Measured data for bottom ash could not be

obtained; consequently the default emission factors for residue only consider fly ash. The data presented in these different studies are in agreement, and the emission factors are assigned a medium confidence level.

## 1g Destruction of Animal Carcasses

Animal carcasses accumulate in quantities sufficient to require large-scale disposal as a result of disease outbreaks in beef and dairy herds, intensive poultry- and hog-raising facilities, veterinary hospitals and practices, etc. The incineration of animal carcasses to reduce public exposure to zoonotic disease is often carried out in simple, low technology, poorly controlled furnaces. As a result, incomplete combustion is the norm rather than the exception. Thus, it is virtually impossible to describe a typical animal carcass-burning furnace. These furnaces are often not designed to guarantee well-controlled combustion conditions nor a high removal efficiency of particulate matter to reduce PCDD/PCDF air emissions.

Destruction of animal carcasses via open burning is addressed in Group 6 – Open Burning Processes.

### Emission Factors

PCDD/PCDF emission factors for three classes of animal carcass incinerators are listed in Table II.1.9. Detailed information on how these emission factors have been derived can be found in Annex 15.

### Guidance for Classification of Sources

For selection of the most appropriate emission factors, the range of animal carcass incineration technologies is divided into three classes:

**Class 1** includes older, batch-fed furnaces with no APC systems.

**Class 2** includes updated, continuously-fed and controlled facilities that are equipped with some APC systems.

**Class 3** includes modern state-of-the-art, continuously-fed and controlled facilities with full APC systems capable of meeting emission limits equivalent to 0.1 ng TEQ/Nm<sup>3</sup> (at 11% O<sub>2</sub>).

**Table II.1.9 PCDD/PCDF emission factors for source category 1g Destruction of Animal Carcasses**

1g	Destruction of Animal Carcasses	Emission Factors (µg TEQ/t animal carcasses incinerated)	
		Air	Residue
1	Older furnaces, batch type operation, no APCS	500	ND
2	Updated, continuously operated and controlled facilities, some APCS	50	ND
3	Modern state-of-the-art facilities, continuous controlled operation, full APCS	5	ND

### Activity rates

Activity rates for animal carcass incineration may be available from

- Ministry of agriculture
- State, provincial, national and/or international agencies that gather centralized statistical information, including large-scale disease outbreaks, such as bird flu, swine flu, bovine encephalopathy, etc., and the associated generation and treatment of animal carcasses;

- State, provincial and national agencies that issue permits to animal carcass incinerators;
- Owner/operators of animal carcass incineration facilities (by questionnaires);
- Other release inventories such as the inventory of criteria pollutants and/or greenhouse gases;
- Pollution Release and Transport Registers (PRTR).
- International statistics such as EUROSTAT, OECD, World Bank etc.

### **Level of Confidence**

No data were found for assigning default emission factors for residues. Based on the scope and agreement of existing air emission data sets for classes 1, 2 and 3, the emission factors are assigned a medium confidence level.

## 2 – Ferrous and Non-Ferrous Metal Production

The iron and steel industry and the non-ferrous metal industry are highly material and energy intensive industries. Considerable amounts of the mass input become outputs in the form of releases to air and residues. The most relevant emissions are those to air. Further, secondary materials and reuse and recycling of solid residues constitute a large part of the industries' activities. Ores and concentrates contain quantities of metals other than the prime target metal, and processes are designed to obtain pure target metal and recover other valuable metals as well. These other metals tend to concentrate in the residues from the process, and in turn, these residues form the raw material for other metal recovery processes. Lastly, filter dusts can be recycled within the same plant or used for the recovery of other metals at other non-ferrous metal installations, by a third party or for other applications.

Primary metallurgical processes are understood to be those aimed at obtaining metals such as iron, copper, aluminum, lead, zinc, etc., from their original ores, whether sulfidized or oxidized through such processes as concentration, smelting, reduction, refining, etc. Secondary metallurgical processes utilize scrap metals, often coated with plastics, paints, used batteries (for lead productions), oils, etc., or slags and fly ash from metallurgical or other processes as raw materials for their processes. In this chapter, the term "primary" metal production is only applied when no used or waste material enters into the process as the metal source.

PCDD/PCDF are relevant to the production of metals. In particular, the production from secondary raw materials has been recognized as a source of PCDD/PCDF. In addition, processes that need chlorination such as the electrolytic production of magnesium from seawater and dolomite may generate PCDD/PCDF (see source category 2i). PCDD/PCDF or their precursors may be present in some raw materials and enter the process, or are newly formed from short-chain hydrocarbons via *de novo* synthesis in furnaces or abatement systems. PCDD/PCDF are easily adsorbed onto solid matter and may be collected and subsequently removed by air pollution control systems. A detailed description of the particular metallurgical processes and the related abatement techniques is given in the BAT&BEP Guidelines.

Since the formation of PCDD/PCDF and other unintentional POPs are thought to originate through high temperature thermal metallurgical processes, hydrometallurgical processes are not considered as PCDD/PCDF sources in this Toolkit, and thus, their releases do not have to be estimated when preparing the national PCDD/PCDF release inventory.

In this section, the Toolkit addresses the following source categories (Table II.2.1):

**Table II.2.1 Overview of source categories included in group 2 - Ferrous and Non-Ferrous Metal Production**

2 - Ferrous and Non-Ferrous Metal Production		Potential release route				
		Air	Water	Land	Product	Residue
a	Iron ore sintering	X				x
b	Coke production	X	x	x	x	x
c	Iron and steel production and foundries	X				x
d	Copper production	X	x			x
e	Aluminum production	X				x
f	Lead production	X				x



g	Zinc production	X				x
h	Brass and bronze production	X				x
i	Magnesium production	x	x			x
j	Other non-ferrous metal production	x	x			x
k	Shredders	X				x
l	Thermal wire reclamation	X	(x)	x		x

With relevance to the provisions of Article 5, sources in these categories can be classified as follows:

**Table II.2.2 Relevance to Article 5, Annex C of the Stockholm Convention**

No	Toolkit source category	Part II	Part III	Relevant source category in Annex C
2a	Iron ore sintering	X		Sinter plants in the iron and steel industry
2b	Coke production		X	Thermal processes in the metallurgical industry not mentioned in Part II
2d	Copper production	X		Secondary copper production
2e	Aluminum production	X		Secondary aluminum production
2f	Lead production		X	Thermal processes in the metallurgical industry not mentioned in Part II
2g	Zinc production	X		Secondary zinc production
2h	Brass and bronze production		X	Thermal processes in the metallurgical industry not mentioned in Part II
2i	Magnesium production		X	Thermal processes in the metallurgical industry not mentioned in Part II
2j	Other non-ferrous metal production		X	Thermal processes in the metallurgical industry not mentioned in Part II
2k	Shredders		X	Shredder plants for the treatment of end of life vehicles
2l	Thermal wire reclamation		X	Smoldering of copper cables

An example of elaborating source inventory and release estimate for this source group is included in the example inventory 3.

## 2a Iron Ore Sintering

Sinter plants are associated with iron manufacture, often in integrated iron and steel mills. The sintering process is a pre-treatment step in the production of iron where fine particles of metal ores are agglomerated by combustion. A detailed description of the iron sintering processes and the related abatement techniques is given in the BAT&BEP Guidelines.

The waste gas flow from a sinter plant varies from 350,000 to 1,600,000 Nm<sup>3</sup>/hour, depending on the plant size and operating conditions. Typically the specific waste gas flow is between 1,500 and 2,500 Nm<sup>3</sup>/t of sinter (BREF 2012). Waste gases are usually treated by dust removal in a cyclone, electrostatic precipitator, wet scrubber or fabric filter. In plants where high PCDD/PCDF emissions have been identified, high performance scrubbing systems may be installed to reduce emissions, coupled with measures to reduce gas flows.

Extensive research into formation of PCDD/PCDF in the sintering process has shown that they are formed within the sinter bed itself, probably just ahead of the flame front as hot gases are drawn through the bed. It has also been shown that *de novo* formation of PCDD/PCDF in the gas collectors from reactive fine dust particles is responsible for approximately 10% of the total PCDD/PCDF and that primary measures to prevent PCDD/PCDF formation should be taken in the sinter bed. Besides input-related measures, disruptions to flame front propagation, *i.e.* non-steady state operations, result in higher PCDD/PCDF emissions (Nordsieck *et al.* 2001). Thus, operating the sintering process as consistent as possible in terms of strand speed, bed composition, bed height, use of additives, and keeping the strand, ductwork and ESP air tight to minimize, as far as possible, the amount of air ingress in the operation will result in less PCDD/PCDF formation.

### Emission Factors

PCDD/PCDF emission factors for three source classes are listed in Table II.2.3. Revised or newly added emission factors are highlighted in red. Emission factors for other unintentional POPs are listed in Annex 16. Detailed information on how default emission factors have been derived can also be found in Annex 16.

### Guidance for classification of sources

**Class 1** includes plants with high use of waste, including cutting oils or other chlorinated contaminants, and limited process control and no or limited air pollution control system.

**Class 2** should be applied for those plants that show good combustion control and have little use of waste, in particular cutting oils.

**Class 3** should be used for those plants which have taken comprehensive measures to control PCDD/PCDF and comply with the BAT&BEP Guidelines.

Very low technology sintering plants may have higher emissions. Any plants found with poor combustion controls and very limited air pollution control systems should be noted for future examination.

**Table II.2.3 PCDD/PCDF emission factors for source category 2a Iron Ore Sintering**

2a	Iron Ore Sintering	Emission Factors (µg TEQ/t sinter produced)				
		Air	Water	Land	Product	Residue*
1	High waste recycling including oil contaminated materials, no or limited air pollution control system	20	ND	ND	NA	0.003
2	Low waste use, well controlled plant	5	ND	ND	NA	<b>1</b>
3	High technology emission reduction	0.3	ND	ND	NA	<b>2</b>

\* Residues: these emission factors are based on an assumption of 0.05 kg dust/t sinter released (*i.e.*, not internally recycled).

## Activity rates

Activity rates may be obtained from various sources, such as the following:

- Owners/operators of the relevant facilities (by questionnaires);
- State, provincial, national and/or international agencies that gather centralized statistical information, including iron and steel production;
- State, provincial and national agencies that issue permits;
- Other release inventories such as the inventory of mercury sources and releases, criteria pollutants and/or greenhouse gases;
- International statistics such as EUROSTAT, OECD, FAO, World Bank, etc.

## Level of Confidence

PCDD/PCDF emission factors for iron ore sintering are provided:

- With a high level of confidence for class 2 and class 3 air emissions, as emission factors are derived from a broad geographical coverage and are based on a low data range and not on expert judgment;
- With a medium level of confidence for class 1 air emissions and class 3 residue releases, as emission factors are based on a low data range and not on expert judgment but are not derived from a broad geographical coverage;
- With a low level of confidence for class 1 and 2 residues releases, as emission factors are based on extrapolations and expert judgment.

## 2b Coke Production

Coke is produced from hard coal or brown coal by carbonization (heating under vacuum). In “coke ovens”, coal is charged into large vessels, which are subjected to external heating to approximately 1,000°C in the absence of air. Coke is removed and quenched with water. The major use of coke is in the iron and steel industry.

No data are available to estimate releases from the production of charcoal from wood. This process can be carried out in many small units, which taken together may represent a considerable production. For initial estimates of emissions, the emission factors given in this section for simple plants should be applied (class 1).

### Emission Factors

PCDD/PCDF emission factors for two source classes are listed in Table II.2.4. Revised or newly added emission factors are highlighted in red. Emission factors for other unintentional POPs are listed in Annex 17. Detailed information on how default emission factors have been derived can also be found in Annex 17.

### *Guidance for classification of sources*

**Class 1** should be applied to facilities where no dust removal device is in use.

**Class 2** should be used for plants using technology such as an afterburner and dust removal equipment.

**Table II.2.4 PCDD/PCDF emission factors for source category 2b Coke Production**

2b	Coke Production	Emission Factors ( $\mu\text{g TEQ/t}$ coke produced)				
		Air	Water	Land	Product	Residue
1	No gas cleaning	3	0.06*	NA	ND	ND
2	APC with afterburner/dust removal	<b>0.03</b>	0.06*	NA	ND	ND

\* Use factor of 0.006  $\mu\text{g TEQ/t}$  where water treatment is applied.

### Activity rates

Activity rates may be obtained from various sources, such as the following:

- Owners/operators of the relevant facilities (by questionnaires);
- State, provincial, national and/or international agencies that gather centralized statistical information, including iron and steel production;
- State, provincial and national agencies that issue permits;
- Other release inventories such as the inventory of mercury sources and releases, criteria pollutants and/or greenhouse gases;
- International statistics such as EUROSTAT, OECD, FAO, World Bank, etc.

### Level of Confidence

For coke production, PCDD/PCDF emission factors are provided with a medium level of confidence for all classes, as emission factors are based on a low data range, they are not based on expert judgment, but are derived from a limited geographical coverage.

## 2c Iron and Steel Production, Foundries and Hot-Dip Galvanizing Plants

The iron and steel industry is a highly material intensive industry with raw materials such as ores, pellets, scrap, coal, lime, limestone (in some cases also heavy oil and plastics) and additives and auxiliaries. It is also highly energy-intensive. More than half of the mass input becomes outputs in the form of releases to air and solid wastes or by-products. The most relevant emissions are those to air, with the emissions from sinter plants dominating the overall emissions for most pollutants (see source category 2a).

In this section, all processes used in the manufacture of iron and steel are covered. Four routes are currently used for the production of steel: the classic blast furnace/basic oxygen furnace route, direct melting of scrap (electric arc furnace), smelting reduction and direct reduction (BREF 2012). For the purpose of the Toolkit, a categorization can be done according to the type of input material: blast furnaces (BF) are used only for the production of pig iron and are fed with iron ores from either sintering plants or pelletizing plants. Blast furnaces do not utilize scrap. Scrap is being used in electric arc furnaces (EAF), Basic Oxygen Furnaces (BOF) as well as in foundries where cupola furnaces (CF) and induction furnaces (IF) are found.

The hot-dip galvanizing process is included in this section since its objective is to protect steel from corrosion.

Five types of furnaces are commonly used to melt metals in foundries: cupola, electric arc, induction, reverberatory, and crucible. As no information is currently identified regarding foundry processes for die casting of non-ferrous metal alloys, which include induction furnaces, reverberatory or crucible

for instance, emission factors of the “iron foundries” section may be used as default factors for such non-ferrous foundry processes.

The various furnace types and processes are described in the BAT&BEP Guidelines.

### Emission Factors

PCDD/PCDF emission factors for eleven source classes grouped by activity type are listed in Table II.2.5. Revised or newly added emission factors are highlighted in red. Emission factors for other unintentional POPs are listed in Annex 18. Detailed information on how default emission factors have been derived can also be found in Annex 18.

#### Guidance for classification of sources

##### In the iron and steel making category:

**Class 1** includes all iron and steel making processes (such as electric arc furnaces and open hearth furnaces), except basic oxygen furnaces and blast furnaces, using dirty scrap containing cutting oils or plastic materials and plants with scrap preheating and relatively poor controls;

**Class 2** includes all iron and steel making processes (such as electric arc furnaces and open hearth furnaces), except basic oxygen furnaces and blast furnaces, using dirty scrap or clean scrap or virgin iron that are fitted with some after-burners and fabric filters for gas cleaning;

**Class 3** includes electric arc furnaces using dirty scrap or clean scrap or virgin iron and efficient gas cleaning with secondary combustion and fabric filters (sometimes in combination with a rapid water quench), and basic oxygen furnaces;

**Class 4** should be used for blast furnaces with air pollution control systems.

##### In the iron foundries category:

**Class 1** includes cold air cupolas or hot air cupola or rotary drum furnaces without fabric filters or equivalent for gas cleaning;

**Class 2** includes rotary drum furnaces with fabric filters or wet scrubbers;

**Class 3** includes cold air cupolas with fabric filters or wet scrubbers;

**Class 4** includes hot air cupolas and induction furnaces fitted with fabric filters or wet scrubbers.

##### In the hot-dip galvanizing plants category:

**Class 1** includes facilities without air pollution control systems;

**Class 2** includes facilities with good air pollution control systems but without a degreasing step;

**Class 3** includes facilities with both air pollution control systems and a degreasing step.

**Table II.2.5 PCDD/PCDF emission factors for source category 2c Iron and Steel Production Plants**

2c	Iron and Steel Production Plants	Emission Factors (µg TEQ/t LS)				
		Air	Water	Land	Product	Residue
<b>Iron and Steel Making</b>						
1	Dirty scrap (cutting oils, general contamination), scrap preheating, limited controls	10	ND	NA	NA	15

2	Clean scrap/virgin iron or dirty scrap, afterburner and fabric filter	3	ND	NA	NA	15
3	Clean scrap/virgin iron or dirty scrap, EAF equipped with APC designed for low PCDD/PCDF emission, BOF furnaces	0.1	ND	NA	NA	<b>0.1</b>
4	Blast furnaces with APCS	0.01	ND	NA	NA	ND
<b>Iron Foundries</b>						
1	Cold air cupola or hot air cupola or rotary drum with no gas cleaning	10	NA	NA	NA	ND
2	Rotary Drum - fabric filter or wet scrubber	4.3	NA/ND*	NA	NA	0.2
3	Cold air cupola – fabric filter or wet scrubber	1	NA/ND*	NA	NA	8
4	Hot air cupola or induction furnace and fabric filter or wet scrubber	0.03	NA/ND*	NA	NA	0.5
<b>Hot-dip Galvanizing Plants Emission Factors (<math>\mu\text{g TEQ/t}</math> galvanized iron/steel)</b>						
1	Facilities without APCS	0.06	NA	NA	NA	<b>0.01</b>
2	Facilities without degreasing step, good APCS (bagfilters)	0.05	NA	NA	NA	<b>2</b>
3	Facilities with degreasing step, good APCS (bagfilters)	0.02	NA	NA	NA	<b>1</b>

\* ND where wet scrubbers are used

### Activity rates

Activity rates may be obtained from various sources, such as the following:

- Owners/operators of the relevant facilities (by questionnaires);
- State, provincial, national and/or international agencies that gather centralized statistical information;
- State, provincial and national agencies that issue permits;
- Other release inventories such as the inventory of mercury sources and releases, criteria pollutants and/or greenhouse gases;
- International statistics such as EUROSTAT, OECD, FAO, World Bank, etc.

### Level of Confidence

For iron and steel making, emission factors for PCDD/PCDF are provided:

- With a high level of confidence for air emissions (all classes) and for class 2 residue releases, as emission factors are derived from a broad geographical coverage and are based on a low data range and not on expert judgment;
- With a medium level of confidence for residue releases related to classes 1 and 3, as emission factors are not based on expert judgment but are not derived from a broad geographical coverage.

For iron foundries, emission factors for PCDD/PCDF are provided:

- With a medium level of confidence for air emissions and for class 4 residue releases, as emission factors are not based on expert judgment but are not derived from a broad geographical coverage;
- With a low level of confidence for class 2 and 3 residue releases, as emission factors are based on extrapolations and expert judgment.

For hot-dip galvanizing plants, emission factors for PCDD/PCDF are provided:

- With a medium level of confidence for air emissions, as emission factors are not based on expert judgment but are not derived from a broad geographical coverage;
- With a low level of confidence for residue releases, as emission factors are based on extrapolations and expert judgment.

## **2d Copper Production**

Thermal copper (Cu) generation and releases of PCDD/PCDF are of special interest, as copper is the most efficient metal to catalyze the formation of PCDD/PCDF. When analyzing the copper production sector for PCDD/PCDF releases, it is important to differentiate between primary and secondary production.

### **Primary copper**

Primary copper may be produced by two different technologies depending on the type of minerals treated, either oxides or sulfides, and from primary concentrates and other materials either by pyrometallurgical or hydrometallurgical routes (BREF 2009). Hydrometallurgical methods are applied to treat oxidized minerals, *i.e.* leaching, solvent extraction, and electrowinning. All these processes are operated at temperatures below 50°C. It is not expected that formation of PCDD/PCDF will occur.

Typically, sulfurized minerals are treated by the pyrometallurgical route. Sulphidic minerals are first treated in a concentration plant, operated at room temperature, and then the concentrates are pyrometallurgically refined in primary copper smelters. The concentrates to be smelted consist basically of copper and iron sulfides and are low in chlorine (ppm). The stages involved are roasting, smelting, converting, refining, and electrorefining. The smelting process is performed in an oxidizing atmosphere at temperatures between 1,200°C and 1,300°C. Further process details are described in the BAT&BEP Guidelines.

### **Secondary copper**

Secondary copper is produced by pyrometallurgical processes and is obtained from scrap or other copper-bearing residues such as slags and ashes. Since used copper can be recycled without loss of quality, secondary copper production is an important sector. An overview of secondary raw materials for copper production and a description of relevant processes can be found in the BAT&BEP Guidelines.

### **Emission Factors**

PCDD/PCDF emission factors for six source classes are listed in Table II.2.6. Revised or newly added emission factors are highlighted in red. In order to harmonize the Toolkit with the BAT&BEP Guidelines, where BAT consideration is given for primary base metal smelters, class 6 - pure primary Cu smelters with no secondary feed materials - is also included in the Toolkit. However, in the absence of measured data, there will be no default emission factor provided for this class.

Emission factors for other unintentional POPs are listed in Annex 19. Detailed information on how default emission factors have been derived can also be found in Annex 19.

### Guidance for classification of sources

**Class 1** should be applied to thermal processing of mixed materials where furnaces are equipped with simple fabric filters, no or less effective air pollution control systems.

**Class 2** will be used where thermal processing of scrap copper materials is carried out in furnaces that are well controlled and fitted, with afterburners and fabric filters. The scrap should undergo some sorting and classification prior to processing to minimize contaminants.

**Class 3** should be used for plants where measures have been taken to address releases of PCDD/PCDF, such as installation of rapid water quench prior to the fabric filters, and activated carbon used in the flue gas treatment.

**Class 4** addresses the smelting and casting of copper and copper alloys.

**Class 5** should be taken for primary Cu, well controlled plants with some secondary feed materials.

**Class 6** includes primary copper smelters that use clean raw materials and use either the base smelting process or the flash smelting. The releases from primary copper smelters that recycled secondary materials such as copper scrap or other residues can be estimated by applying the emission factor for class 5. For this class, the “pure” primary copper smelters, there are no emission factors presently available.

**Table II.2.6 PCDD/PCDF emission factors for source category 2d Copper Production**

2d	Copper Production	Emission Factors (µg TEQ/t copper)				
		Air	Water	Land	Product	Residue
1	Sec. Cu – Basic Technology	800	0.5	NA	NA	630
2	Sec. Cu – Well controlled	50	0.5	NA	NA	630
3	Sec. Cu –Optimized for PCDD/PCDF control	5	0.5	NA	NA	300
4	Smelting and casting of Cu/Cu alloys	0.03	0.5	NA	NA	ND
5	Prim. Cu, well-controlled, with some secondary feed materials	0.01	0.5	NA	NA	ND
6	Pure primary Cu smelter with no secondary feed materials	ND	0.5	NA	NA	NA

### Activity rates

Activity rates may be obtained from various sources, such as the following:

- Owners/operators of the relevant facilities (by questionnaires);
- State, provincial, national and/or international agencies that gather centralized statistical information;
- State, provincial and national agencies that issue permits;
- Other release inventories such as the inventory of mercury sources and releases, criteria pollutants and/or greenhouse gases;
- International statistics such as EUROSTAT, OECD, FAO, World Bank, etc.



## Level of Confidence

For copper production, emission factors for PCDD/PCDF are provided:

- With a high level of confidence for class 2 and 5 air emissions, as emission factors are derived from a broad geographical coverage and are based on a low data range and not on expert judgment;
- With a medium level of confidence for water releases, for classes 1, 3 and 4 air emissions and for classes 2 and 3 residue releases, as emission factors are not based on expert judgment but are not derived from a broad geographical coverage;
- With a low level of confidence for class 1 residue releases, as emission factors are based on extrapolations and expert judgment.

## 2e Aluminum Production

Aluminum (Al) can be produced from aluminum ore, most commonly bauxite (primary production), or from scrap (secondary production). In primary aluminum production, the mined aluminum ore (e.g., bauxite) is refined into aluminum oxide trihydrate (alumina) through the Bayer Process. The alumina is then electrolytically reduced into metallic aluminum through the Hall-Héroult Process, which utilizes either self-baking anodes, the Söderberg anodes, or pre-baked anodes. The use of pre-baked anodes represents the most modern process. Further process information can be found in the BAT&BEP Guidelines.

Primary aluminum production is generally thought not to be a significant source of unintentional POPs. However PCDD/PCDF formation and release is possible through the graphite-based electrodes used in the electrolytic smelting process.

### Emission Factors

PCDD/PCDF emission factors for six source classes are listed in Table II.2.7. Revised or newly added emission factors are highlighted in red. Emission factors for other unintentional POPs are listed in Annex 20. Detailed information on how default emission factors have been derived can also be found in Annex 20.

### Guidance for classification of sources

**Class 1** should be used for plants with simple or no dust removal equipment.

**Class 2** should be used for plants that have scrap pre-treatment, afterburners and dust control (e.g. fabric filters), other air pollution controls but no specific dioxin treatment.

**Class 3** should be used where high efficiency controls are in place consisting of scrap cleaning, afterburners, fabric filters with lime and specific dioxin treatment (activated carbon injection).

**Class 4** applies to the drying of Al shavings and turnings in rotary drums or similar equipment.

**Class 5** applies to thermal de-oiling of turnings in rotary kilns with afterburners and fabric filters.

**Class 6** refers to primary aluminum production by electrolysis and ingot smelting.

**Table II.2.7 PCDD/PCDF emission factors for source category 2e Aluminum Production**

2e	Aluminum Production Classification	Emission Factors (µg TEQ/t aluminum)				
		Air	Water	Land	Product	Residue

1	Thermal processing of scrap Al, minimal treatment of inputs and simple dust removal	100	ND	NA	NA	200
2	Thermal Al processing, scrap pre-treatment, well-controlled, fabric filters with lime injection	3.5	ND	NA	NA	<b>400</b>
3	Optimized for PCDD/PCDF control – afterburners, lime injection, fabric filters and active carbon	0.5	ND	NA	NA	100
4	Shavings/turning drying (simple plants)	5	NA	NA	NA	NA
5	Thermal de-oiling of turnings, rotary furnaces, afterburners, and fabric filters	0.3	NA	NA	NA	NA
6	Pure primary Al production	ND	NA	NA	NA	ND

### Activity rates

Activity rates may be obtained from various sources, such as the following:

- Owners/operators of the relevant facilities (by questionnaires);
- State, provincial, national and/or international agencies that gather centralized statistical information;
- State, provincial and national agencies that issue permits;
- Other release inventories such as the inventory of mercury sources and releases, criteria pollutants and/or greenhouse gases;
- International statistics such as EUROSTAT, OECD, FAO, World Bank, etc.

### Level of Confidence

For aluminum production, emission factors for PCDD/PCDF are provided:

- With a high level of confidence for class 2 air emissions, as emission factors are derived from a broad geographical coverage and are based on a low data range and not on expert judgment;
- With a medium level of confidence for all other classes (air and residue vectors), as emission factors are based on a low data range but are not derived from a broad geographical coverage.

## 2f Lead Production

Two main routes for primary lead production from sulfide ores are available – sintering/smelting and direct smelting. Emissions from direct smelting are low and not considered further (SCEP 1994).

Considerable quantities of lead are recovered from scrap materials, in particular vehicle batteries. A variety of furnace designs are used, including rotary furnaces, reverberatory, crucible, shaft, blast and electric furnaces. Continuous direct smelting processes may be used.

PCDD/PCDF emissions may be linked to high organic matter and the presence of chlorine in scrap materials; in particular, a link between the use of PVC separators in vehicle batteries and PCDD/PCDF emissions has been made.

### Emission Factors

PCDD/PCDF emission factors for four source classes are listed in Table II.2.8. Revised or newly added emission factors are highlighted in red. Emission factors for other unintentional POPs are listed in Annex 21. Detailed information on how default emission factors have been derived can also be found in Annex 21.

#### Guidance for classification of sources

**Class 1** Secondary lead production from scrap containing PVC, no air pollution control system.

**Class 2** Secondary lead production from PVC/Cl<sub>2</sub> free scrap, some air pollution control system.

**Class 3** Lead production from PVC/Cl<sub>2</sub> free scrap in highly efficient furnaces, with air pollution control systems including wet scrubbers.

**Class 4** Pure primary lead production.

**Table II.2.8 PCDD/PCDF emission factors for source category 2f Lead Production**

2f	Lead Production	Emission Factors (µg TEQ/t lead)				
		Air	Water	Land	Product	Residue
	<b>Classification</b>					
1	Lead production from scrap containing PVC	80	ND	NA	NA	ND
2	Lead production from PVC/Cl <sub>2</sub> free scrap, some APCS	8	ND	NA	NA	50
3	Lead production from PVC/Cl <sub>2</sub> free scrap in highly efficient furnaces, with APC including scrubbers	<b>0.05</b>	ND	NA	NA	ND
4	Pure primary lead production	<b>0.4</b>	NA	NA	NA	ND

### Activity rates

Activity rates may be obtained from various sources, such as the following:

- Owners/operators of the relevant facilities (by questionnaires);
- State, provincial, national and/or international agencies that gather centralized statistical information;
- State, provincial and national agencies that issue permits;
- Other release inventories such as the inventory of mercury sources and releases, criteria pollutants and/or greenhouse gases;
- International statistics such as EUROSTAT, OECD, FAO, World Bank, etc.

### Level of Confidence

For lead production, emission factors for PCDD/PCDF are provided:

- With a high level of confidence for class 2 air emissions and residue releases, as emission factors are derived from a broad geographical coverage and are based on a low data range and not on expert judgment;
- With a medium level of confidence for classes 1, 3 and 4 air emissions, as emission factors are based on a low data range but are not derived from a broad geographical coverage.

## 2g Zinc Production

Zinc may be recovered from ores through a variety of processes. The co-occurrence of lead and zinc ores means that there may be a considerable overlap between these two sectors. Crude zinc may be produced in combination with a lead ore blast furnace or be recovered from the slag from such processes in rotary kilns. A variety of scrap materials may be used for zinc recovery as well as secondary raw materials such as dusts from copper alloy production, electric arc steel-making (*e.g.*, filter dusts and sludge), residues from steel scrap shredding, scrap from galvanizing processes. The zinc production process from secondary raw materials can be done in a zinc recovery rotary kiln (Waelz kiln), which is up to 95 m long with internal diameters of around 4.5 m; they are lined with refractory material.

The processing of impure scrap such as the non-metallic fraction from shredders is likely to involve production of pollutants, including PCDD/PCDF. Relatively low temperatures are used to recover lead and zinc (340 and 440°C). Melting of zinc may occur with the addition of fluxes including zinc and magnesium chlorides. Further process information can be found in the BAT&BEP Guidelines.

### Emission Factors

PCDD/PCDF emission factors for four source classes are listed in Table II.2.9. Revised or newly added emission factors are highlighted in red. Emission factors for other unintentional POPs are listed in Annex 22. Detailed information on how default emission factors have been derived can also be found in Annex 22.

### Guidance for classification of sources

**Class 1** Rotary kiln with no air pollution control system.

**Class 2** Hot briquetting/rotary furnaces equipped with basic dust control (*e.g.*, fabric filters/electrostatic precipitators).

**Class 3** Secondary zinc production with comprehensive air pollution control systems (*e.g.*, fabric filters with active carbon/DeDiox technology).

**Class 4** Zinc melting and primary zinc production.

Table II.2.9 PCDD/PCDF emission factors for source category 2g Zinc Production

2g	Zinc Production	Emission Factors (µg TEQ/t zinc)				
		Air	Water	Land	Product	Residue
	<b>Classification</b>					
1	Kiln with no APCS	1,000	ND	NA	NA	<b>0.02</b>
2	Hot briquetting/rotary furnaces, basic dust control; <i>e.g.</i> , fabric filters/ESP	100	ND	NA	NA	<b>1*</b>
3	Comprehensive air pollution controls, <i>e.g.</i> , fabric filters with active carbon/DeDiox	5	ND	NA	NA	<b>1*</b>

	technology					
4	Zinc melting and primary zinc production	0.1	ND	NA	NA	ND

\* In some cases (e.g. Waelz kilns) emission factors can be as high as 2,000 µg TEQ/t of zinc

### Activity rates

Activity rates may be obtained from various sources, such as the following:

- Owners/operators of the relevant facilities (by questionnaires);
- State, provincial, national and/or international agencies that gather centralized statistical information;
- State, provincial and national agencies that issue permits;
- Other release inventories such as the inventory of mercury sources and releases, criteria pollutants and/or greenhouse gases;
- International statistics such as EUROSTAT, OECD, FAO, World Bank, etc.;

### Level of Confidence

For zinc production, emission factors for PCDD/PCDF are provided:

- With a high level of confidence for classes 2 and 3 air emissions, as emission factors are derived from a broad geographical coverage and are based on a low data range and not on expert judgment;
- With a medium level of confidence for other classes and/or vectors, as emission factors are not based on expert judgment but are not derived from a broad geographical coverage.

## 2h Brass and Bronze Production

Brass is a hard yellow shiny metal that is an alloy of copper (55%-90%) and zinc (10%-45%). The properties of brass vary with the proportion of copper and zinc and with the addition of small amounts of other elements, such as aluminum, lead, tin, or nickel. In general, brass can be forged or hammered into various shapes, rolled, etc. Brass can be produced by either re-melting the brass scrap or melting stoichiometric amounts of copper and zinc together. In principle, either one or both can be primary or secondary metal.

Bronze is a hard yellowish-brown alloy of copper and tin, phosphorus, and sometimes small amounts of other elements. Bronze is harder than copper and brass. Bronze is often cast to make statues. Most bronze is produced by melting the copper and adding the desired amounts of tin, zinc, and other substances. The properties of the alloy depend on the proportions of its components.

Brass and bronze can be produced in simple, relatively small melting pots or in more sophisticated equipment such as induction furnaces equipped with air pollution control systems.

### Emission Factors

PCDD/PCDF emission factors for four source classes are listed in Table II.2.10. Emission factors for other unintentional POPs are listed in Annex 23. Detailed information on how default emission factors have been derived can also be found in Annex 23.

### Guidance for classification of sources

**Class 1** should be used for plants which are more elaborated than class 2 furnaces, e.g. induction ovens equipped with baghouse filters and wet scrubbers and/or de-oiling of turnings.

**Class 2** should be used for simple smelting furnaces equipped with some flue gas abatement technology, e.g. scrubber or electrostatic precipitators.

**Class 3** includes induction furnaces using mixed scrap and equipped with fabric filters.

**Class 4** includes more sophisticated equipment such as induction ovens with APCS.

**Table II.2.10 PCDD/PCDF emission factors for source category 2h Brass and Bronze Production**

2h	Brass and Bronze Production	Emission Factors (µg TEQ/t brass/bronze)				
		Air	Water	Land	Product	Residue
1	Thermal de-oiling of turnings, afterburner, wet scrubber	2.5	NA	NA	NA	NA
2	Simple melting furnaces	10	ND	NA	NA	ND
3	Mixed scrap, induction furnaces, fabric filters	3.5	ND	NA	NA	125
4	Sophisticated equipment, e.g. induction ovens with APCS	0.1	ND	NA	NA	ND

### Activity rates

Activity rates may be obtained from various sources, such as the following:

- Owners/operators of the relevant facilities (by questionnaires);
- State, provincial, national and/or international agencies that gather centralized statistical information;
- State, provincial and national agencies that issue permits;
- Other release inventories such as the inventory of mercury sources and releases, criteria pollutants and/or greenhouse gases;
- International statistics such as EUROSTAT, OECD, FAO, World Bank, etc.

### Level of Confidence

For brass and bronze production, emission factors for PCDD/PCDF are provided:

- With a high level of confidence for classes 1, 3 and 4 air emissions, as emission factors are derived from a broad geographical coverage and are based on a low data range and not on expert judgment;
- With a medium level of confidence for other classes and/or vectors, as emission factors are not based on expert judgment but are not derived from a broad geographical coverage.

## 2i Magnesium Production

The production of magnesium from ores is largely based on either electrolysis of MgCl<sub>2</sub> or chemical reduction of oxidized magnesium compounds. The raw materials used are dolomite,

magnesite, carnallite, brines or seawater depending on the process. Magnesium can also be recovered and produced from a variety of magnesium-containing secondary raw materials.

The electrolysis process is more widely used. This process seems to be of most interest from the point of view of PCDD/PCDF formation and release. Secondary magnesium production is not addressed in this section.

In the thermal reduction process, calcined dolomite is reacted with ferro-silicon sometimes together with aluminum in a furnace or retort vessel. The calcination process takes place by decarbonization and dehydration of dolomite limestone. For the calcination process of dolomite, often a rotate or vertical furnace is used. Further process information can be found in the BAT&BEP Guidelines.

### Emission Factors

PCDD/PCDF emission factors for three source classes are listed in Table II.2.11. Emission factors for other unintentional POPs are listed in Annex 24. Detailed information on how default emission factors have been derived can also be found in Annex 24.

#### Guidance for classification of sources

**Class 1** Production processes using MgO and coke thermal treatment in Cl<sub>2</sub> atmosphere, without treatment of wastewater and with limited gas treatment.

**Class 2** Production processes using MgO and coke thermal treatment in Cl<sub>2</sub> atmosphere with comprehensive pollution control.

**Class 3** Thermal reduction process.

**Table II.2.11 PCDD/PCDF emission factors for source category 2i Magnesium Production**

2i	Magnesium Production	Emission Factors (µg TEQ/t magnesium)				
		Air	Water	Land	Product	Residue
1	Production using MgO/C thermal treatment in Cl <sub>2</sub> – no treatment on effluent, limited gas treatment	250	9,000	NA	NA	0
2	Production using MgO/C thermal treatment in Cl <sub>2</sub> – comprehensive pollution control	50	30	NA	NA	9,000
3	Thermal reduction process	3	ND	NA	NA	NA

### Activity rates

Activity rates may be obtained from various sources, such as the following:

- Owners/operators of the relevant facilities (by questionnaires);
- State, provincial, national and/or international agencies that gather centralized statistical information;
- State, provincial and national agencies that issue permits;
- Other release inventories such as the inventory of mercury sources and releases, criteria pollutants and/or greenhouse gases;
- International statistics such as EUROSTAT, OECD, FAO, World Bank, etc.

## Level of Confidence

For magnesium production, emission factors for PCDD/PCDF are provided:

- With a high level of confidence for class 2 air and water releases and for class 3, as emission factors are derived from a broad geographical coverage and are based on a low data range and not on expert judgment;
- With a medium level of confidence for class 2 residue releases and for class 1, as emission factors are not based on expert judgment but are not derived from a broad geographical coverage.

## 2j Other Non-ferrous Metal Production

A number of non-ferrous metals are not assigned to a specific category in the Toolkit: cadmium, precious metals, chromium, nickel, ferro-alloys (FeSi, FeMn, SiMn, etc.), alkali metals, etc. A variety of processes are undertaken to produce and refine non-ferrous metals. The exact processes used and the propensity to form PCDD/PCDF are complex and not studied in detail. It is important not to miss potentially significant PCDD/PCDF sources simply because data are insufficient to provide comprehensive emissions factors. Therefore, to provide an initial indication of potential releases, it is suggested that processes in non-ferrous metal production are examined. Releases may occur to air, water, and in residues. When investigating production processes, it is suggested that thermal processes are noted, the type of gas cleaning system applied recorded, and the levels of contamination found in the input materials noted. The use of Cl<sub>2</sub> or hexachloroethane for refining, and the presence of chlorinated compounds in raw materials should also be noted. The Questionnaire provided in the Toolkit will assist in identifying and recording these parameters.

In the case of these non-ferrous metals, a 3-step approach is proposed:

1. First step: some non-ferrous metals are produced in conjunction with metals which are assigned to a specific category in the toolkit. In that case, the corresponding emission factors should be considered. For example:
  - Cadmium may be produced in conjunction with lead or zinc. Emission factors of category 2f (class 4) or category 2g (class 4) should be considered.
  - Precious metals may be produced in conjunction with copper or lead. Emission factors of category 2d (classes 5 or 6) or category 2f (class 4) should be considered.
2. Second step: some non-ferrous metals are produced in processes similar to other processes which are assigned to a specific category or class in the toolkit. In that case, the corresponding emission factors should be considered. For example, ferro-alloys are usually produced in electric arc furnaces similar to those used in the iron and steel sector, hence emission factors of category 2c should be considered. Another example are zinc alloys (*e.g.* zamak) which can be produced similarly to bronze and brass. Therefore, emission factors of category 2h, if appropriate classes apply, can be used as default values.
3. Finally, if a given non-ferrous metal cannot be considered under the first or the second step, emission factors of category 2j should be used.



## Emission Factors

PCDD/PCDF emission factors for two source classes are listed in Table II.2.12. Detailed information on how these emission factors have been derived can be found in Annex 25.

### Guidance for classification of sources

**Class 1** Thermal non-ferrous metal processes utilizing contaminated scrap with simple or no air pollution control systems.

**Class 2** Thermal non-ferrous metal processes utilizing clean scrap and air pollution control systems such as fabric filters, lime injection and afterburners.

**Table II.2.12 PCDD/PCDF emission factors for source category 2j Other Non-Ferrous Metal Production**

2j	Other Non-Ferrous Metal Production Classification	Emission Factors ( $\mu\text{g TEQ/t product}$ )				
		Air	Water	Land	Product	Residue
1	Thermal non-ferrous metal processes – contaminated scrap, simple or no APCS	100	ND	NA	NA	ND
2	Thermal non-ferrous metal processes – clean scrap, fabric filters/lime injection/afterburners	2	ND	NA	NA	ND

### Activity rates

Activity rates may be obtained from various sources, such as the following:

- Owners/operators of the relevant facilities (by questionnaires);
- State, provincial, national and/or international agencies that gather centralized statistical information;
- State, provincial and national agencies that issue permits;
- Other release inventories such as the inventory of mercury sources and releases, criteria pollutants and/or greenhouse gases;
- International statistics such as EUROSTAT, OECD, FAO, World Bank, etc.

### Level of Confidence

For other non-ferrous metals production, emission factors for PCDD/PCDF are provided with a low level of confidence, as they are based on expert judgment and are not derived from a broad geographical coverage. However, given the wide range of situations (raw materials, industrial processes) under this source category, emission factors may be process-specific.

## 2k Shredders

When talking about shredders, usually automobile shredders are mentioned. Other feedstock is also accepted; in practice, much light scrap such as bicycles, office furniture, vending machines and so-called “white” goods, *e.g.*, refrigerators, stoves, washing machines, etc., and “brown” goods, *e.g.*, television sets, radios, etc., are fed into shredders (Nijkerk and Dalmijn 2001). Shredders are large-scale machines, which are equipped inside with one or more anvil(s) or breaker bar(s) and lined with alloy steel wear plates. Details on the process can be found in the BAT&BEP Guidelines.

Shredder plants for treatment of end of life vehicles are listed in Annex C of the Convention as a source that has the potential to form and release unintentional POPs. However, at present there is not sufficient evidence that in this mechanical process PCDD/PCDF or PCB are newly formed. The data available indicate that PCDD/PCDF and PCBs released from shredder plants are from industrial/intentional PCB production and have been introduced with oils, dielectric fluids, etc. contained in such vehicles or consumer goods. The shredders simply set free these contaminants.

Based on this information, one single class of emission factors is used for releases from the shredding process itself.

### **Emission Factors**

PCDD/PCDF emission factors for one source class are listed in Table II.2.13. Revised or newly added emission factors are highlighted in red. PCB emission factors are listed in Annex 26. Detailed information on how default emission factors have been derived can also be found in Annex 26.

**Table II.2.13 PCDD/PCDF emission factors for source category 2k Shredders**

2k	Shredders	Emission Factors (µg TEQ/t recovered steel)				
		Air	Water	Land	Product	Residue
1	Metal shredding plants	0.2	NA	NA	ND	<b>5</b>

### **Activity rates**

Activity rates may be obtained from various sources, such as the following:

- Owners/operators of the relevant facilities (by questionnaires);
- State, provincial, national and/or international agencies that gather centralized statistical information;
- State, provincial and national agencies that issue permits;
- Other release inventories such as the inventory of mercury sources and releases, criteria pollutants and/or greenhouse gases;
- International statistics such as EUROSTAT, OECD, FAO, World Bank, etc.

### **Level of Confidence**

For shredders, PCDD/PCDF emission factors to air are provided with a high level of confidence, as they are derived from a broad geographical coverage and are based on a low data range and not on expert judgment. PCDD/PCDF emission factors for residues releases are provided with a low level of confidence, as they are based on extrapolations and expert judgment.

## **21 Thermal Wire Reclamation and E-Waste Recycling**

Burning of cable is the process in which copper is recovered from wire by burning the insulating material. In its most basic form, this process takes place in the open and consists of scrap wire, which is burned to remove wire coverings. In many countries this would be considered to be an illegal operation. More sophisticated operations would use a furnace with gas clean-up consisting of afterburners and scrubbers. In this process, all ingredients to form PCDD/PCDF are present: carbon (sheath), chlorine (PVC or mould resistant agents) and a catalyst (copper).

## Emission Factors

PCDD/PCDF emission factors for four source classes are listed in Table II.2.14. Revised or newly added emission factors are highlighted in red. Emission factors for other unintentional POPs are listed in Annex 27. Detailed information on how default emission factors have been derived can also be found in Annex 27.

### Guidance for classification of sources

**Class 1** includes open burning of wire, not conducted at dedicated industrial sites related to category 2d.

**Class 2** includes factors for open burning of circuit boards, especially in the case of e-waste recycling.

**Class 3** factors should be used for controlled operations to recover wire using a furnace with basic gas cleaning, *i.e.*, for cable burning in furnaces fitted with afterburners and wet scrubbers.

**Class 4** factors should be used for furnaces used to recover electric motor windings, brake shoes and the like with some gas cleaning system fitted.

**Table II.2.14 PCDD/PCDF emission factors for source category 2I Thermal Wire Reclamation and E-Waste Recycling**

2I	Thermal Wire Reclamation and E-Waste Recycling	Emission Factors ( $\mu\text{g TEQ/t material}$ )				
		Air	Water	Land	Product	Residue
	<b>Classification</b>					
1	Open burning of cable	12,000	ND	ND	ND	ND
2	Open burning of circuit boards	100	ND	ND	ND	ND
3	Basic furnace with afterburner and wet scrubber	40	ND	NA	ND	ND
4	Burning electric motors and brake shoes, etc. – afterburner fitted	3.3	ND	NA	ND	ND

### Activity rates

It may be necessary to estimate the amount of wire burned in the open since it is unlikely that statistics will be kept. Sites where this process occurs can usually be identified due to the residue that remains.

### Level of Confidence

For thermal wire reclamation and e-waste recycling, emission factors for PCDD/PCDF and for PCB are provided with a medium level of confidence, as emission factors are not based on expert judgment but are not derived from a broad geographical coverage.

### 3 – Power Generation and Heating

This source group includes power stations, industrial firing places (furnaces) and installations for providing space heating, which are fired with fossil fuels (including up to 1/3 co-combustion of waste), biogas including landfill gas, and biomass only. Table II.3.1 outlines the five categories within this source group. The main release vectors are air and residue. Land is considered as a release vector only in the case of domestic heating and cooking using either biomass (mostly wood) or fossil fuels. Releases to land can occur if residues are dumped on the ground.

As generation of heat or power is the aim of these plants, in the case of the combustion of biomass or fossil fuels, the amount of PCDD/PCDF cannot easily be equated to mass (in tons) or energy input (in Joule) of fuel burned. The preferred basis to report emissions of PCDD/PCDF would be the energy input of the fuel. As the heat or power output is the “product” of the processes in this group, the default emission factors derived from the available data are linked to the heating value of the fuel. Thus, instead of reporting default emission factors in µg TEQ/t of fuel, these factors are given in µg TEQ/TJ of heat input. The reason for this approach is the high variety of fuels used for power generation. The range of heating values of various coals from various parts of the world stretches over more than one order of magnitude. To recalculate heating values into masses, conversion tables are provided in Annex 28.

**Table II.3.1 Overview of source categories included in group 3 - Power Generation and Heating**

3 - Power Generation and Heating		Potential release route				
		Air	Water	Land	Product	Residue
a	Fossil fuel power plants (coal, oil, gas, shale oil, and co-combustion of waste)	x				x
b	Biomass power plants (wood, straw, other biomass)	x				x
c	Landfill, biogas combustion	x				x
d	Household heating and cooking with biomass (wood, other biomass)	x		(x)		x
e	Household heating and cooking with fossil fuels (coal, oil, gas)	x		(x)		x

**Table II.3.2 Relevance to Article 5, Annex C of the Stockholm Convention**

No	Toolkit source category	Part II	Part III	Relevant source category in Annex C
1a	Fossil fuel power plants (coal, oil, gas, shale oil, and co-combustion of waste)	X		Co-incinerators of waste
1a	Fossil fuel power plants (coal, oil, gas, shale oil, and co-combustion of waste)		X	Fossil fuel fired utility and industrial boilers
1b	Biomass power plants (wood, straw, other biomass)	X		Co-incinerators of waste
1b	Biomass power plants (wood, straw, other biomass)		X	Firing installations for wood and biomass

1c	Landfill, biogas combustion	X		Co-incinerators of waste
1d	Household heating and cooking with biomass (wood, other biomass)	X		Co-incinerators of waste
1d	Household heating and cooking with biomass (wood, other biomass)		X	Residential combustion sources
1e	Household heating and cooking with fossil fuels (coal, oil, gas)	X		Co-incinerators of waste
1e	Household heating and cooking with fossil fuels (coal, oil, gas)		X	Residential combustion sources
1e	Household heating and cooking with fossil fuels (coal, oil, gas)		X	Fossil fuel fired utility and industrial boilers

An example of elaborating source inventory and release estimate for this source group is included in the example inventory 4.

### 3a Fossil Fuel Power Plants

Six classes are defined within this category according to the types of fuels used, namely coal, heavy fuel oil, shale fuel oil, peat, light fuel oil and natural gas, as well as any type of fossil fuel in a combination with the co-combustion of any kind of waste or sludge. For all classes, it is assumed that reasonably well-operated and maintained power steam generators are employed in order to maximize power output. In all cases, air and residue are the only release vectors under consideration.

Fossil fuel is burned in a wide array of devices for power generation ranging from small stoker fired furnaces to large and highly sophisticated boiler/burner systems with extensive air pollution control plants at the back end. Coal combustion for power generation takes place in two general types of boilers distinguished by the way the ash is extracted from the system. The so-called dry bottom boilers use stokers or pulverized coal burners arranged in an opposed wall, which burn coal in a highly efficient manner leaving the majority of the ash as a dry residue at the bottom of the boiler. The so-called wet bottom boilers use pulverized burners in a cyclone or U-fired arrangement, which leads to much higher combustion temperatures resulting in the ash melting and collected as a liquid slag at the bottom of the boiler. Typical flue gas cleaning devices for large coal-fired power plants consist of units for NO<sub>x</sub> control (*e.g.* SCR technology), particulate matter control (*e.g.* electrostatic precipitators) and desulphurization (*e.g.* lime stone scrubbing). These devices can reduce PCDD/PCDF emissions as a side effect.

Heavy fuel oil is also combusted for power generation purposes. It is usually burned in specially designed burners incorporated in the boiler walls. The formation of PCDD/PCDF is favored during co-combustion of liquid or sludge wastes such as waste oil and/or used solvents.

Light fuel oil and natural gas are always fired in specially designed burners and are not likely to generate large amounts of PCDD/PCDF since both are highly calorific, clean burning fuels with little or no ash at all. Only if liquid or sludge waste is co-fired, higher releases of PCDD/PCDF may be formed.

In some countries such as Australia, Brazil, Canada, China, Estonia, France, Russia, United Kingdom (in Scotland), South Africa, Spain, Sweden, and the USA large quantities of oil shale exist, which can be

converted to shale oil, a substance similar to petroleum. In Estonia, for example, more than 90% of the country's electricity is generated from shale oil (Schleicher 2004a). In some countries peat is a domestic energy resource and is used for heat and/or power generation, *e.g.* in Finland or Ireland (McGettigan *et al.* 2009).

Like in all combustion processes, PCDD/PCDF are usually formed after the combustion process is completed and the flue gas cools down. The remaining soot particles and the chlorine contained in the coal recombine in the presence of the metal-chloride catalysts to form PCDD/PCDF. Releases to water, land and product are normally negligible. Major release routes are to air and residue, especially to fly ash. Releases to water may occur at plants where wet scrubbers are installed, where water is not recirculated within the scrubbers. In such cases, releases to water have to be included. Sludge from such scrubbers, when separated from the effluents, will occur under "Residues". In the case of wet limestone scrubbing for desulfurization, the resulting gypsum is used in building industries and may be considered as "Product".

In some countries, catalysts are marketed for the combustion of soot and boiler cleaning. These catalysts contain copper salts and lead to a significant increase of PCDD/PCDF formation to air and residues. Measurements from Poland show an increase of emissions in such cases by a factor of 1,000.

### **Emission Factors**

PCDD/PCDF emission factors for six source classes are listed in Table II.3.3. The emission factors apply to the operation of boilers in general and therefore include the combined heat and power production as well as the production of heat only. Revised or newly added emission factors are highlighted in red. Detailed information on how these emission factors have been derived can be found in Annex 30.

### **Guidance for classification of sources**

The classification of sources is according to the type of fossil fuel used. A further split depending on the size and type of technology in place is not proposed here due to lack of reliable information. Such a split may be introduced at the national level depending on available data. The source allocation shall fit to the corresponding activity rates (see below). Therefore, national energy statistics and their source category split are essential for source classification.

**Class 1** For the co-firing of waste, the allocation to this class depends on the main purpose of the process (here: heat and power generation, not waste incineration). Co-firing usually occurs with solid fuels (coal, lignite) together with sewage sludge, biomass, organic waste from industry or other waste-derived fuels. The co-combustion of different types of gases (*e.g.* coke oven gas and blast furnace gas) is not considered here. The combustion of sewage sludge together with liquid fuels or natural gas should be allocated to waste incineration.

**Class 2** The emission factors refer to the combustion of hard coal. In case of information lacking at the national level, this factor may be transferred to lignite fired boilers. Emission factors can be significantly higher in the case of unfavorable combustion conditions (Grochowalski and Konieczynski 2008, see Annex 30).

**Class 3** The emission factor refers to peat combustion in boilers for heat and/or power production. Peat is used in countries where it is domestically available.

**Class 4** The emission factor refers to heavy fuel oil combustion in boilers for heat and/or power production. Heavy fuel oil is a fraction from mineral oil refining with standardized properties. Residual oils or other residues from the refining process are not considered here.

**Class 5** The emission factor refers to shale oil combustion in boilers for heat and/or power production. Shale oil is used in countries where it is domestically available.

**Class 6** The emission factor refers to the combustion of natural gas or light fuel oil in boilers for heat and/or power production. This factor may be transferred to the combustion in gas turbines or in combined cycle power plants as well.

**Table II.3.3 PCDD/PCDF emission factors for source category 3a Fossil Fuel Power Plants**

3a	Fossil Fuel Power Plants	Emission Factors ( $\mu\text{g TEQ/TJ}$ fossil fuel burned)				
		Air	Water	Land	Product	Residue
1	Fossil fuel/waste co-fired power boilers	35*	ND	NA	NA	ND
2	Coal fired power boilers	10**	ND	NA	NA	14
3	Peat fired power boilers	17.5	ND	NA	NA	ND
4	Heavy fuel fired power boilers	2.5	ND	NA	NA	ND
5	Shale oil fired power boilers	1.5	ND	NA	NA	***
6	Light fuel oil/natural gas fired power boilers	0.5	ND	NA	NA	ND

\* including co-firing of biomass (range: 30-50  $\mu\text{g TEQ/TJ}$ )

\*\* high range depending on fuel quality and combustion conditions (3-100  $\mu\text{g TEQ/TJ}$ )

\*\*\* Releases with residues can be calculated on a mass basis (see Annex 30, Section on Release in Residues)

### Activity rates

The activity rates for this category can be derived from national energy statistics. For PCDD/PCDF release estimates, only a split according to the fuel type is proposed in the Toolkit. Combustion in boilers for heat and/or power production occurs in various economic sectors. Here, energy industries are the most important ones. In other industrial sectors, combustion may occur in boilers or in other types of process furnaces which need to be distinguished (*e.g.* drying of products, other heating furnaces). A detailed knowledge of technologies in place may be necessary for an appropriate allocation of the energy input to such processes. The respective industries' associations may provide such information.

Co-firing of waste usually cannot be found in energy statistics, which only include the total amount of incinerated waste. In most cases, the actual quantity needs to be directly collected from the power plant operators. If no statistical data exist, estimates may be based on a smaller sample at the local scale, with an extrapolation of results to the whole country.

### Level of confidence

The levels of confidence were assigned based on a lack of knowledge of the sources and the variability of the emissions from a given source. The latter is linked to fuel quality and operating conditions. The variability of emissions becomes lower with higher fuel quality (*e.g.* natural gas compared to co-firing of waste) and optimized plant operation (*e.g.* large power plants compared to small boilers). The level of confidence is high for natural gas (due to high range of data from many



literature results, high variability of emissions observed) and decreases to low for solid fuels, in particular for the co-firing of waste (low geographical coverage).

The results should be cross-checked with regard to the consistency of the overall inventory (share of the sector in total emissions; per capita emissions compared to countries with a similar structure).

### **3b Biomass Power Plants**

Many countries and regions are heavily dependent on the combustion of biomass for power and heat production. Biomass fuels may include wood including twigs, bark, saw dust, wood shavings, peat, and/or agricultural residue (*e.g.*, straw, citrus pellets, coconut shells, poultry litter, camel excretes, etc.). In most cases, biomass is burned directly and without any addition of fossil fuels in small, continuously operated steam boilers. For the Toolkit, four classes are defined within this category according to the type of biomass used, namely wood-fired boilers using clean wood or mixed biomass, and other types of herbaceous biomass-fired boilers, namely straw and other agricultural residues. Agricultural residues like straw or rice husk are an important fuel type in many countries. This herbaceous biomass often has higher chlorine content compared to wood, leading to problems during combustion (*e.g.* slagging) but also to potentially higher formation of PCDD/PCDF. Therefore emission factors are distinguished from those for wood combustion.

For all classes, it is assumed that reasonably well-operated and maintained power steam generators are employed in order to maximize power output. In all cases, air and residue are the only release vectors. This category does not address firing of contaminated wood waste, which is covered by category 1f Waste Wood and Waste Biomass Incineration.

Biomass is burned in a wide array of devices for power generation ranging from small stoker fired furnaces to large and highly sophisticated boiler/burner systems with extensive air pollution control plants at the back end. The various types of biomass furnaces with typical applications and fuels are presented in the BAT&BEP Guidelines.

#### **Emission Factors**

PCDD/PCDF emission factors for four source classes are listed in Table II.3.4. Revised or newly added emission factors are highlighted in red. Detailed information on how these emission factors have been derived can be found in Annex 31.

#### ***Guidance for classification of sources***

**Class 1** includes boilers firing wood waste which is not contaminated by paints or coatings. In some countries, classifications of wood waste exist which refer to the level of contamination. Here, mixed biomass refers to the category characterizing low contamination. This type of wood waste is frequently used in CHP boilers *e.g.* in wood industries. Incineration of contaminated wood waste shall be allocated to category 1f (waste wood and waste biomass incineration).

**Class 2** includes boilers firing log wood, wood chips or pellets as a high quality fuel allowing optimized combustion conditions.

**Class 3** includes boilers firing straw for heat or power production. Straw-fired boilers need to be adapted to this fuel with regard to ash properties (slagging) and combustion conditions.



**Class 4** includes boilers firing various types of herbaceous biomass such as rice husk or bagasse. Especially in Asian countries a wide range of agricultural residues is used for heat generation. Nevertheless, information on PCDD/PCDF emissions from this source is still scarce.

**Table II.3.4 PCDD/PCDF emission factors for source category 3b Biomass Power Plants**

3b	Biomass Power Plants	Emission Factors ( $\mu\text{g TEQ/TJ biomass burned}$ )				
		Air	Water	Land	Product	Residue*
1	Mixed biomass fired power boilers	500	ND	NA	NA	ND
2	Clean wood fired power boilers	50	ND	NA	NA	15
3	Straw fired boilers	50	ND	NA	NA	70
4	Boilers fired with bagasse, rice husk, etc	50**	ND	NA	NA	50

\*Total of bottom ash and fly ash

\*\* Estimate based on straw combustion, Thailand: Installation with APC (ESP, cyclones, Venturi scrubbers): ca. 20  $\mu\text{g TEQ/TJ}$

### Activity rates

Biomass used for heat and power generation should be indicated in the national energy statistics. Nevertheless, biomass is frequently merged with other fuels and allocation to the four classes will require additional information such as the installed capacity of biomass-fired boilers, statistics on agricultural production and waste statistics. Additional assumptions may be necessary such as the share of straw used for energy recovery.

### Level of confidence

In class 2 the level of confidence is high with high quality fuels burned in good operation conditions (clean wood), due to the wide range of data and availability of many literature results. Low confidence is linked with class 4, for which fuels are not well defined, operating conditions may be unknown and experimental data on PCDD/PCDF emissions is scarce. For classes 1 and 3 the level of confidence is estimated medium due to lower data range.

## 3c Landfill Biogas Combustion

Landfill gas and biogas are both generated from anaerobic digestion of organic matter. The resulting gas is a mixture of carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), and ammonia (NH<sub>3</sub>), and smaller fractions of combustible gases as well as a large fraction of water (H<sub>2</sub>O). The combustible portion of the gas is usually around 50% and the heating value is 15–25 MJ/kg depending on the origin of the gas. The combustion of landfill gas and biogas either occurs in a flare, in gas motors or turbines and other power generating devices.

The combustion of these gases for power generation takes place predominantly in either gas-fired boilers or gas motors/turbines. Both systems closely resemble to those firing natural gas. The combustion process is virtually residue-free.

### Emission Factors

One PCDD/PCDF emission factor for a single source class is listed in Table II.3.5. Detailed information on how this has been derived can be found in Annex 32.

### Guidance for classification of sources

**Class 1** This class includes the combustion of biogas resulting from anaerobic digestion (see above).

**Table II.3.5 PCDD/PCDF emission factors for source category 3c Landfill Biogas Combustion**

3c	Landfill Biogas Combustion	Emission Factors ( $\mu\text{g TEQ/TJ gas burned}$ )				
		Air	Water	Land	Product	Residue
1	Boilers, motors/turbines, flaring	8	ND	NA	NA	NA

### Activity rates

This class includes various activities requiring different sources of information:

- Landfill gas: Information may be included in the national statistic on waste treatment. The number of landfills with a gas capture system should be known as well as the average annual gas production depending on the age of the landfill.
- Biogas from waste treatment: This activity includes sewage sludge treatment as well as the digestion of the organic fraction of municipal waste. Activity rates should be reported in national waste treatment statistics.
- Biogas from agricultural plants: This activity includes dedicated biogas facilities for renewable energy generation. These plants are using maize or other crop together with liquid manure. Information on this activity should be found in renewable energy statistics or in communications from respective associations.

### Level of confidence

The quality of the biogas (and potentially the variability of emissions) depends on the origin of the gas. Landfill gas may have contaminants from volatile compounds of the surrounding waste leading to higher POPs emissions. Gas quality can be better controlled in dedicated installations *e.g.* for the digestion of agricultural residues. The assigned LoC is medium, due to limited number of datasets available.

## 3d Household Heating and Cooking with Biomass

Heating and cooking with biomass in residential households is a common practice in many countries. In most cases the fuel of preference is wood, however, other biomass fuels may be used such as straw, peat, etc. Six individual classes are defined within this category, with the main difference being the quality of the fuel and the appliances used. This differentiation comes from the need for representing simple stoves or 3-stone stoves which are widely used especially in developing countries. Air, residue, and in some cases land are the release vectors under consideration.

Biomass for residential heating and cooking is burned in a wide array of devices ranging from small, open pit stoves and fireplaces to large and highly sophisticated wood burning stoves and ovens. The latter are addressed in the “advanced technology” class. The combustion of biomass for household heating and cooking takes place predominantly in devices of increasing combustion efficiency as the gross national product and the state of development of individual countries increase.

PCDD/PCDF are formed as a result of incomplete combustion, typical in these small devices with no or limited combustion controls. Releases to water and product are negligible. Releases to land can occur only if the combustion process takes place directly on the ground (this case is addressed in Group 6 - Open Burning Processes) or when residues are disposed of to the land. Thus, the only significant release routes are to air, land, and residue.

Recent studies showed comparatively low emission factors for open fire simple stoves (Cardenas *et al.* 2011). Nevertheless, simple stoves can lead to high exposure rates with negative impacts on human health through indoor air pollution.

In some countries, catalysts are marketed for the combustion of soot and boiler cleaning. These catalysts contain copper salts and lead to a significant increase of PCDD/PCDF formation to air and residues. Measurements from Poland show an increase of emissions in such cases by a factor of 1,000 (Grochowalski 2010, 2012).

### Emission Factors

PCDD/PCDF emission factors for six source classes are listed in Table II.3.6. Revised or newly added emission factors are highlighted in red. Emission factors for other unintentional POPs are listed in Annex 33. Detailed information on how default emission factors have been derived can also be found in Annex 33.

Residues from biomass combustion are generated with a rate of 0.5 – 5% per mass of biomass burned. Ash contents for different types of wood vary from 0.1 up to 3%. Details on various types of wood can be found in Annex 28.

### Guidance for classification of sources

**Class 1** includes all types of stoves firing contaminated biomass such as wood waste, painted wood, etc. The actual emissions will depend on the degree of contamination and the combustion conditions.

**Class 2** includes ovens and stoves with controlled air supply and optimized combustion conditions firing virgin wood. This class applies usually to residential heating with biomass in modern appliances. Lower emissions are expected from automatic furnaces using wood chips or pellets.

**Class 3** applies to all types of residential combustion using herbaceous biomass as a fuel such as straw. In case of mixed fuels (*e.g.* wood and straw) the class with the higher emission factor shall apply.

**Class 4** applies to all types of residential combustion using charcoal as a fuel.

**Class 5** applies to residential combustion of wood without control of combustion conditions and without ducts for the evacuation of flue gases. Traditional 3-stone stoves are a typical example.

**Class 6** applies to simple stoves for heating or cooking with limited combustion control and with a duct for the evacuation of flue gases.

**Table II.3.6 PCDD/PCDF emission factors for source category 3d Household Heating and Cooking with Biomass**

3d	Household Heating and Cooking with Biomass	Emission Factors (µg TEQ/TJ biomass burned)				Concentration (ng TEQ/kg ash)
		Air	Water	Land	Product	Residue
1	Contaminated biomass fired stoves	1,500	ND	ND	NA	1,000
2	Virgin biomass fired stoves (advanced technology)	100	ND	ND	NA	10
3	Straw fired stoves	450	ND	ND	NA	30
4	Charcoal fired stoves	100*	ND	ND	NA	0.1

5	Open-fire 3-stone stoves (virgin wood)	20**	ND	ND	NA	0.1
6	Simple stoves (virgin wood)	100	ND	ND	NA	0.1

\* Preliminary expert estimate; Emissions from barbecuing are not included.

\*\* Expert estimate derived from a field test in Mexico (Cardenas *et al.* 2011)

### Activity rates

Biomass use in the residential sector is often not covered by statistical data. Especially informal wood markets are not registered. If possible local studies should be conducted on the amount of biomass used, as well as technologies in place. Results from such studies may be extrapolated to the national level. In case of absence of such data, results from countries with similar structure may be transferred *e.g.* via per capita consumption of biomass. The use of waste in residential appliances is an illegal practice in many countries. Here, expert estimates have to be made to quantify emissions from this source. Some countries have developed case studies on this topic and results may be used as a first indication.

### Level of confidence

There are multiple sources of uncertainty associated with the emissions from the residential sector. Activity rates are uncertain due to incomplete coverage of statistical data (see above). PCDD/PCDF emissions are strongly dependent on fuel quality and combustion conditions. Both parameters are largely varying and are often unknown at the national level. Therefore, the level of confidence is estimated low for all classes (due to limited data availability but wide range of values) except class 2 with clean fuel and controlled combustion conditions (confidence: medium). For the latter, emission factors are derived based on many studies available, including a wide range of values.

## 3e Household Heating and Cooking with Fossil Fuels

Fossil fuel is used extensively for domestic heating, especially in developed countries and in countries with economies in transition. Coal, (light fuel) oil and (natural) gas are the main sources of fossil fuel used for domestic heating. For these three classes, it is assumed that reasonably well-operated and maintained heating ovens are employed in order to maximize heat output. In the case of co-firing of waste and/or biomass, combustion conditions may degrade due to lower fuel quality. In all cases, air is the release vector under consideration. In the case of coal combustion, residue must also be considered as a potential release vector.

Fossil fuel is burned in devices ranging from small stoker fired furnaces to large elaborate highly sophisticated boiler/burner systems for central heat generation in large multi unit residential buildings.

Combustion for domestic heating takes place in two general types of boilers distinguished by the way the heat is transported and released. The so-called central heating systems, which use oil or gas as a fuel, include one large furnace to heat water, which then is circulated through the building to release its heat in numerous decentralized radiators. These modern systems are typically highly efficient and fairly clean, leaving little or no residue for disposal. The second type of heating system is mostly based on solid fuels (coal) and consists of individual stoves, which are located in each room of the building or inside the wall to provide direct access to several rooms at the same time. These stoves consist of fairly small furnaces but provide a system for air to circulate inside the stove around the furnace. These systems are typically older, less efficient and less clean. In addition, bottom ash

resulting from the inert content of the fuel is generated and must be disposed of. Some of these systems are also capable of burning oil.

In some countries catalysts are marketed for the combustion of soot and boiler cleaning. These catalysts contain copper salts and lead to a significant increase of dioxin formation for both release routes air and residues. Measurements from Poland show an increase of emissions in such cases by a factor of 1,000.

### Emission Factors

PCDD/PCDF emission factors for six source classes are listed in Table II.3.7. Revised or newly added emission factors are highlighted in red. Detailed information on how these emission factors have been derived can be found in Annex 34.

### Guidance for classification of sources

**Class 1** applies to domestic stoves firing coal with high chlorine content (chlorine salt content above 0.5% mass). High chlorine salt contents are a specific property of certain domestic coals. Information on properties of coals and briquettes marketed in a country for domestic use needs to be taken into account.

**Class 2** applies to domestic stoves using mixed solid fuels. In most cases this category applies to the simultaneous or alternating firing of coal and biomass. Nevertheless, co-firing of waste in residential appliances is an illegal practice in many countries.

**Class 3** applies to domestic stoves, ovens and boilers firing coal or coal briquettes with low chlorine content.

**Class 4** applies to domestic stoves, ovens and boilers firing peat. The use of peat as a fuel in the residential sector is closely linked to its local availability.

**Class 5** applies to domestic stoves, ovens and boilers firing light fuel oil. The use of heavy oil fractions in the residential sector is often banned.

**Class 6** applies to domestic stoves, ovens and boilers firing natural gas. The same factor can be applied to light petroleum gas and similar fractions.

**Table II.3.7 PCDD/PCDF emission factors for source category 3e Household Heating and Cooking with Fossil Fuels**

3e	Household Heating and Cooking with Fossil Fuels	Emission Factors ( $\mu\text{g TEQ/TJ}$ fossil fuel burned)				Concentration (ng TEQ/kg ash)
		Air	Water	Land	Product	Residue
1	High chlorine coal/waste/biomass co-fired stoves	<b>1,700*</b>	ND	NA	NA	<b>5,000</b>
2	Coal/waste/biomass co-fired stoves	<b>200</b>	ND	NA	NA	NA
3	Coal fired stoves	100	ND	NA	NA	<b>5</b>
4	Peat fired stoves	<b>100</b>	ND	NA	NA	NA
5	Oil fired stoves	10	ND	NA	NA	NA
6	Natural gas fired stoves	1.5	ND	NA	NA	NA

\*Pandelova *et al.* 2005

### **Activity rates**

Classes 1, 2, 3, 5 and 6 are usually covered by national energy statistics. Information on coal properties may be available from associations of coal suppliers or from case studies on this topic. Specific investigations may be necessary to quantify domestic peat consumption as it may be produced in an artisanal way. Expert estimates have to be made to quantify emissions from the combustion of mixed solid fuels. Energy statistics do not address the share of co-firing in total fuel consumption. The use of waste in residential appliances is an illegal practice in many countries. Some countries have nevertheless developed case studies on this topic and results may be used as a first indication.

### **Level of confidence**

In this category, the level of uncertainty is directly linked with the fuel quality. The level of confidence is high in the case of natural gas combustion (class 6). This is due to the use of clean fuel and high stability of the process. Low confidence levels can be attributed to the combustion of mixed solid fuels in particular in the case of co-firing of waste (classes 1 and 2), due to the low stability of the process and wide range of data. Medium levels are estimated for classes 3, 4 and 5, due to the better defined fuel composition but wide range of data.

## 4 – Mineral Products

This section summarizes high-temperature processes in the mineral industry. Raw materials or fuels that contain chlorides may potentially cause the formation of PCDD/PCDF at various steps of the processes, *e.g.*, during the cooling phase of the gases or in the heat zone. Due to the long residence time in kilns and the high temperatures needed for the product, emissions of PCDD/PCDF are generally low in these processes. The categories shown in Table II.4.1 will be included into the dioxin and furan inventory.

**Table II.4.1 Overview of source categories included in group 4 - Mineral Products**

4 - Mineral Products		Potential release route				
		Air	Water	Land	Product	Residue
a	Cement production	X				x
b	Lime production	X				x
c	Brick production	X				x
d	Glass production	X				x
e	Ceramics production	X				x
f	Asphalt mixing	X			x	x
g	Oil shale pyrolysis	X				x

With relevance to the provisions of Article 5, sources in this category can be classified as follows:

**Table II.4.2 Relevance to Article 5, Annex C of the Stockholm Convention**

No	Toolkit source category	Part II	Part III	Relevant source category in Annex C
4a	Cement production	X		Cement kilns firing hazardous waste

An example of elaborating source inventory and release estimate for this source group is included in the example inventory 5.

### 4a Cement Production

Principal raw materials for cement production are clay and limestone. There are four main process routes for the manufacture of cement: the dry, semi-dry, semi-wet and wet processes. These processes are described in detail in the BAT&BEP Guidance.

Modern cement kilns often use the dry process, in which raw mill material may be pre-heated in a vertically arrayed multi-cyclone pre-heater, in which the rising hot gases exiting the kiln contact the downward flowing raw materials. Some dry processes also employ a pre-calciner stage just before the raw material enters the kiln. The use of the wet process, where the ground meal is mixed with water and fed into the kiln uses about 40% more energy than the dry process. Semi-dry and semi-wet processes use grate pre-heaters, also known as Lepol kilns.

Typical fuels used are coal, oil, gas or petroleum coke. In many cases a variety of alternative fuels derived from high calorific wastes are also used to supplement the fossil fuel. The wastes may include: waste oils, solvents, animal meals, certain industrial wastes, and in some cases hazardous wastes. Most of these will be fired at the burner (hot) end of the kiln. Tires are often used and may be added to the kiln as whole tires or chipped.

## Emission Factors

PCDD/PCDF emission factors for four source classes are listed in Table II.4.3. As can be seen, there is no emission factor for releases with residues. Typically, cement kilns do not generate residues since the ESP dust is reintroduced into the process and releases via this vector are negligible. Some cement kilns with a high input of chlorine (from wastes or raw materials) have a bypass installed to separate high chlorine containing Cement Kiln Dust (CKD; up to 10% chloride) before the first cyclone. Typically this CKD is sent to specific landfills or underground mines. More information on how process outputs are managed can be found in the BAT&BEP Guidelines. Detailed information on how emission factors have been derived can be found in Annex 35.

### Guidance for classification of sources

**Class 1** includes shaft kilns.

**Class 2** includes old wet kilns and with dust collectors operating at temperatures above 300°C.

**Class 3** includes modern rotary kilns, where the dust collector is between 200 and 300°C.

**Class 4** includes modern plants where dust collector temperatures are held below 200°C.

**Table II.4.3 PCDD/PCDF emission factors for source category 4a Cement Production**

4a	Cement Production Classification	Emission Factors (µg TEQ/t cement produced)				
		Air	Water	Land	Product	Residue
1	Shaft kilns	5	ND	NA	ND	ND
2	Old wet kilns, ESP temperature > 300°C	5	ND	NA	ND	ND
3	Rotary kilns, ESP/FF temperature 200-300°C	0.6	ND	NA	ND	ND
4	Wet kilns, ESP/FF temperature < 200°C Dry kilns preheater/precalciner, T < 200°C	0.05	ND	NA	ND	ND

### Activity rates

Activity rates may be obtained from various sources, such as the following:

- Owners/operators of the relevant facilities (by questionnaires);
- State, provincial, national and/or international agencies that gather centralized statistical information, including cement production;
- State, provincial and national agencies that issue permits;
- Other release inventories such as the inventory of heavy metals, criteria pollutants and/or greenhouse gases;
- International statistics such as EUROSTAT, OECD, FAO, World Bank, etc.

### Level of Confidence

The emission factors are based on data available from various regions of the world, and are thus assigned a high confidence level.

## 4b Lime Production

Lime is used in a wide range of products. Quicklime (or burnt lime) is calcium oxide (CaO) produced by decarbonization of limestone (CaCO<sub>3</sub>). Slaked lime is quicklime with water content and



mainly consists of calcium hydroxide (Ca(OH)<sub>2</sub>). Major users of lime are the steel industry, construction, pulp and sugar industries.

The lime making consists of the burning of calcium and/or magnesium carbonate at a temperature between 900 and 1,500°C. For some processes, higher temperatures are needed. The calcium oxide product (CaO) from the kiln is generally crushed, milled, and/or screened before being conveyed into a silo. The burned lime is either delivered to the end user in the form of quicklime or reacted with water in a hydrating plant to produce hydrated lime or slaked lime.

Different fuels - solid, liquid, or gaseous - are used in lime burning. Most kilns can operate on more than one fuel. The lime burning process involves two phases (BREF 2010):

1. Providing sufficient heat at above 800°C to heat the limestone and cause decarbonization, and
2. Holding the quicklime at sufficiently high temperatures (around 1,200-1,300°C) to adjust reactivity.

Most of the kilns are either shaft or rotary design. Most kilns are characterized by the counter-current flow of solids and gases. Fluidized bed kilns and rotary hearths may also be found. The typical kiln sizes are between 50 and 500 tons per day (BREF 2010).

### Emission Factors

PCDD/PCDF emission factors for two source classes are listed in Table II.4.4. Detailed information on how these emission factors have been derived can be found in Annex 36.

### Guidance for classification of sources

**Class 1** includes plants with poorer combustion and simple or no gas cleaning systems.

**Class 2** includes kilns are highly energy efficient and fitted with fabric filter gas cleaning.

**Table II.4.4 PCDD/PCDF emission factors for source category 4b Lime Production**

4 b	Lime Production	Emission Factors (µg TEQ/t lime produced)				
		Air	Water	Land	Product	Residue
1	No dust control or contaminated, poor fuels	10	NA	NA	ND	ND
2	Lime production using dust abatement	0.07	NA	NA	ND	ND

### Activity rates

Activity rates may be obtained from various sources, such as the following:

- Owners/operators of the relevant facilities (by questionnaires);
- State, provincial, national and/or international agencies that gather centralized statistical information, including lime production;
- State, provincial and national agencies that issue permits;
- Other release inventories such as the inventory of criteria pollutants and/or greenhouse gases.

## Level of Confidence

The way the kiln inputs are controlled and maintaining a stable kiln operation is an important factor impacting PCDD/PCDF releases. Emission factors for less controlled processes such as those of class 1 are assigned a medium level of confidence. The emission factor in class 2 is assigned a high level of confidence due to better control of the process and available data.

## 4c Brick Production

Brick production with simple kilns, ranging from informal to industrial dimensions, is an important activity in developing and emerging countries. The installations present in various parts of the world have different characteristics. For instance, industrial scale kilns with a large capacity of production (approximately 100 million tons per year) are encountered in South Africa. In Mexico, typical kilns have significantly lower production capacities (around 100 tons per kiln per year), and most often are concentrated in small areas. Kenyan kilns are small size installations, with the output entirely used for own demand.

Various fuels are used, and especially in emerging economies traditional fuels (wood) are often replaced by wastes with high caloric values (oil, tires, plastic). These fuels may promote higher emissions of PCDD/PCDF, PCB and HCB.

### Emission Factors

PCDD/PCDF emission factors for two source classes are listed in Table II.4.5. The air emission factors for PCDD/PCDF are the same as in the 2005 edition of the Toolkit. However, high levels detected in ash (around 100 ng/kg PCDD/PCDF TEQ) and bricks (around 10 ng/kg) at one Mexican site using a mix of heavy oil and tree bark indicate the need for further investigations to assess whether these data pertain to another class (Umlauf *et al.* 2011). However, with regards the bricks, it can be assumed that PCDD/PCDFs are immobilized to a large extent.

Revised or newly added emission factors are highlighted in red. Emission factors for other unintentional POPs are listed in Annex 37. Detailed information on how default emission factors have been derived can also be found in Annex 37.

### Guidance for classification of sources

**Class 1** factors should be applied to smaller and less controlled kilns with no gas cleaning technology.

**Class 2** includes technologies with no emission abatement in place and using non-contaminated fuels, those using emission abatement and any kind of fuel, and with no emission abatement in place but state of the art process control.

**Table II.4.5 PCDD/PCDF emission factors for source category 4c Brick Production**

4c	Brick Production	Emission Factors (µg TEQ/t brick produced)				
		Air	Water	Land	Product	Residues*
1	No emission abatement in place and using contaminated fuels	0.2 <sup>i</sup>	NA	NA	0.06 <sup>iii</sup>	0.02 <sup>v</sup>
2	No emission abatement in place and using non-contaminated fuels	0.02 <sup>ii</sup>	NA	NA	0.006 <sup>iv</sup>	0.002 <sup>vi</sup>
	Emission abatement in place and using					

	any kind of fuel.					
	No emission abatement in place but state of the art process control**					

\* In countries with no waste management or no reuse of the residue for brick making, this often goes to Land.

\*\* For brick kilns with state of the art process control, such as the Hoffmann type, it has been demonstrated that co-incineration of waste does not promote emissions of PCDD/PCDF when compared to the use of coal (Ubaque *et al.* 2010).

<sup>i</sup> Confirmed/derived with field measurements at Mexican artisanal brick kilns using waste oil

<sup>ii</sup> Confirmed/derived with field measurement at Mexican Kilns using virgin wood

<sup>iii</sup> Derived from field measurements at Mexican artisanal brick kilns using waste oil

<sup>iv</sup> Derived from coal and virgin wood fired brick kilns in Mexico, South Africa at industrial and artisanal scale

<sup>v</sup> Derived from Mexican artisanal brick kilns fired with contaminated fuels

<sup>vi</sup> Derived from virgin wood and coal fired kilns in Mexico, South Africa and Kenya at industrial and artisanal scale

### Activity rates

Activity rates may be obtained from various sources, such as the following:

- Owners/operators of the relevant facilities (by questionnaires);
- State, provincial, national and/or international agencies that gather centralized statistical information;
- State, provincial and national agencies that issue permits;
- State, regional or national construction and commerce chambers;
- Other release inventories such as the inventory of heavy metals, criteria pollutants and/or greenhouse gases;
- IPCC databases may be also considered to assess activity rates;
- Energy efficiency programs and projects databases may help to assess activity rates and identify implementation of upgraded kilns. Because of recent interest in controlling emission of black carbon, changes in brick production may happen towards more efficient and even emission control in the kilns (UNEP 2011a).

Additional guidance on estimating activity rates for artisanal brick production is included in the example inventory 5.

### Level of Confidence

No other reports from artisanal kilns have been produced regarding POPs. The data used to derive the emission factors to air were produced via two experiments with partial geographical coverage. Emission factors to land and residues have a broader coverage. In particular, kilns typical to China and other Asian countries were not assessed. Because of energy efficiency programs, continuous types of kilns are being implemented in Asia, Africa and in the near future in Latin America. Based on the above, the level of confidence assigned to emission factors for class 1 is high to medium, and for class 2 is medium.

## 4d Glass Production

Furnaces used for glass manufacture may be continuously or intermittently operated. Typical fuels are oil and gas. The raw materials are principally sand, limestone, dolomite, soda and in some cases recycled glass. In addition a wide range of other materials may be used to achieve desired properties such as color, clarity, and for purification. Chlorinated and fluorinated compounds may be added (SCEP 1994). In some modern glass furnaces, gases are cleaned with sorbents and electrostatic precipitators or fabric filters.

### Emission Factors

PCDD/PCDF emission factors for two source classes are listed in Table II.4.6. Detailed information on how these emission factors have been derived can be found in Annex 38.

### Guidance for classification of sources

**Class 1** includes furnaces with no dust controls which use poor, contaminated fuels.

**Class 2** includes furnaces using dust abatement.

**Table II.4.6 PCDD/PCDF emission factors for source category 4d Glass Production**

4d	Glass Production	Emission Factors ( $\mu\text{g TEQ/t product}$ )				
		Air	Water	Land	Product	Residue
	<b>Classification</b>					
1	No dust control or contaminated, poor fuels	0.2	NA	NA	ND	ND
2	Glass production using dust abatement	0.015	NA	NA	ND	ND

### Activity rates

Activity rates may be obtained from various sources, such as the following:

- Owners/operators of the relevant facilities (by questionnaires);
- State, provincial, national and/or international agencies that gather centralized statistical information, including glass production;
- State, provincial and national agencies that issue permits;
- Other release inventories such as the inventory of heavy metals, criteria pollutants and/or greenhouse gases.

### Level of Confidence

Emission factors are provided with a medium level of confidence, based on the limited geographical scope of available data.

## 4e Ceramics Production

There is not enough information available to consider the production of ceramics as a source of PCDD/PCDF. As ceramics production is a thermal process, PCDD/PCDF will most likely be released to air. An estimate of these releases can be made by applying the emission factors developed for brick making.

## 4f Asphalt Mixing

Asphalt is generally used for road construction, and consists of rock chips, sand, fillers bound together in bitumen. Fillers can include fly ash from incineration or power plants.

The first stage of the process is generally an air-drying unit for the minerals. The hot minerals are then mixed with hot bitumen to obtain asphalt. Asphalt mixing plants in industrialized countries may typically have gas cleaning such as fabric filters or wet dust control devices.

### Emission Factors

PCDD/PCDF emission factors for two source classes are listed in Table II.4.7. Detailed information on how these emission factors have been derived can be found in Annex 39.

### Guidance for classification of sources

**Class 1** includes installations without gas cleaning systems or using poor or contaminated fuels.

**Class 2** includes modern asphalt mixing installations fitted with fabric filter or wet scrubbers for gas cleaning.

**Table II.4.7 PCDD/PCDF emission factors for source category 4f Asphalt Mixing**

4f	Asphalt Mixing	Emission Factors ( $\mu\text{g TEQ/t asphalt mix}$ )				
		Air	Water	Land	Product	Residue
	<b>Classification</b>					
1	Mixing plant with no gas cleaning, poor fuels	0.07	NA	NA	ND	ND
2	Mixing plant with fabric filter or wet scrubber	0.007	NA	NA	ND	0.06

### Activity rates

Activity rates may be obtained from various sources, such as the following:

- Owners/operators of the relevant facilities (by questionnaires);
- State, provincial, national and/or international agencies that gather centralized statistical information, including on road construction;
- Oil refineries producing asphalt.

### Level of Confidence

Emission factors are provided with a medium level of confidence, based on the limited geographical scope of available data.

## 4g Oil Shale Processing

Oil shale is a general term applied to a group of fine black to dark brown shales rich enough in bituminous material (called kerogen) to yield petroleum upon distillation. The kerogen in oil shale can be converted to oil through pyrolysis. During pyrolysis the oil shale is heated to 500°C in the absence of air and the kerogen is converted to oil and separated out, a process called "retorting".

The term "oil shale" is a misnomer. It does not contain oil nor is it commonly shale. The organic material is chiefly kerogen and the "shale" is usually a relatively hard rock, called marl. Properly processed, kerogen can be converted into a substance somewhat similar to petroleum. However, oil

shale was not converted into “oil” by natural processes and therefore, oil shale has to be heated to a high temperature to become fossil fuel (WEC 2004).

There are two conventional approaches to oil shale processing (WEC 2004): in the first one, the shale is fractionated in-situ and heated to obtain gases and liquids. The second approach is by mining, transporting, and heating the shale to about 450°C, adding hydrogen to the resulting product, and disposing of and stabilizing the waste.

Oil shale has been burned directly as a fuel in a few countries such as Estonia, whose energy economy remains dominated by shale. For emission factors in the oil shale fired power plants, see source category 3a Fossil Fuel Power Plants.

### **Emission Factors**

PCDD/PCDF emission factors for two source classes are listed in Table II.4.8. Detailed information on how these emission factors have been derived can be found in Annex 40.

### **Guidance for classification of sources**

**Class 1** includes thermal fractionation process.

**Class 2** includes oil shale pyrolysis.

**Table II.4.8 PCDD/PCDF emission factors for source category 4g Oil Shale Processing**

4g	Oil Shale Processing	Emission Factors (µg TEQ/t oil shale)				
		Air	Water	Land	Product	Residue
	<b>Classification</b>					
1	Thermal fractionation (process 1)	ND	ND	ND	ND	ND
2	Oil shale pyrolysis	0.003	NA	ND	0.07	2

### **Activity rates**

Activity rates may be obtained from various sources, such as the following:

- State, provincial, national and/or international agencies that gather centralized statistical information;
- National energy balance;
- Owners/operators of the relevant facilities (by questionnaires);
- State, provincial and national agencies that issue permits.

### **Level of Confidence**

Emission factors are provided with a medium level of confidence, based on the limited geographical scope of available data.

## 5 – Transport

POPs emissions from transport (road and off-road vehicles) result from incomplete combustion of fuel in engines. Levels of PCDD/PCDF and other unintentional POPs in exhaust gases from vehicles depend on many factors including the type of engine, its maintenance condition and age, technologies of emission reduction applied (catalysts), type and quality of fuel, driving conditions, ambient conditions etc. The assessment of the impacts of these factors on releases is very important, especially when considering the growth in the number of cars. For the purpose of developing a PCDD/PCDF emission inventory, a simple methodology can be used, where PCDD/PCDF emission rates are considered as a function of the type of engine and type of fuel. The impact of these two parameters on PCDD/PCDF concentrations in exhaust gases are among the most studied. Thus, Toolkit emission factors are given according to the type of combustion engine, the type of fuel, and the emission reduction technology applied (catalysts).

Four source categories are included in this group (see Table II.5.1): 4-stroke engines (gasoline fueled engines with spark ignition), 2-stroke engines (gasoline fueled engines with spark ignition), Diesel engines (Diesel fueled engines with compression ignition), and heavy oil fueled engines (mostly turbines). These types of engines are dominant in the transport sector. In addition, other types of engines are also used such as Wankel rotary engines, gas generators etc. These are nevertheless less frequent and may be included into the existing Toolkit categories.

The major fuels used in road transportation are gasoline and Diesel. In smaller volumes, other types of fuels such as liquefied petroleum gas (LPG), compressed natural gas (CNG), liquid biofuels (ethanol, methanol, biodiesel) and hydrogen are used. Their market is growing but, so far, no dioxin measurements are available. In order to accommodate releases from these fuels, the following hypotheses are proposed:

- For LPG-fuelled cars: take the emission factor for 4-stroke engines with catalyst (5a3);
- For oil/gas or oil/gasoline mixtures: the emission factor for Diesel should be applied (5c1).

As for air transport, the occurrence of PCDD/PCDF has not been reported from aircrafts. Increases in concentrations or changes in patterns of PCDD/PCDF could not be detected in a biomonitoring program at the Frankfurt International Airport on long-term exposure of kale at different locations, *i.e.*, along the runway or close to the terminals. Consequently, it was assumed that the combustion of kerosene in aircraft motors is not a source of PCDD/PCDF and this category is not addressed in the Toolkit (Fiedler *et al.* 2000a, Buckley-Golder *et al.* 1999).

**Table II.5.1 Overview of source categories included in group 5 - Transport**

5 - Transport		Potential release route				
		Air	Water	Land	Product	Residue
a	4-Stroke engines	X				
b	2-Stroke engines	X				
c	Diesel engines	X				(x)
d	Heavy oil fired engines	X				(x)

With relevance to the provisions of Article 5, sources in this category can be classified as follows:

**Table II.5.2 Relevance to Article 5, Annex C of the Stockholm Convention**

No	Toolkit source category	Part II	Part III	Relevant source category in Annex C
5a	4-Stroke engines		X	Motor vehicles, particularly those burning leaded gasoline
5b	2-Stroke engines		X	Motor vehicles, particularly those burning leaded gasoline
5c	Diesel engines		X	Motor vehicles, particularly those burning leaded gasoline
5d	Heavy oil fired engines		X	Motor vehicles, particularly those burning leaded gasoline

An example of elaborating source inventory and release estimate for this source group is included in the example inventory 6.

## 5a 4-Stroke Engines

Most gasoline powered internal combustion engines used today in cars, light trucks, motorcycles and other vehicles are 4-stroke engines. These engines follow the thermodynamic combustion cycle invented by Nicolaus Otto, which consists of 4 strokes, namely the intake stroke, the compression stroke, the ignition and combustion stroke, and the exhaust stroke. These four strokes are completed during two full revolutions of the crankshaft. Like all combustion processes, internal combustion engines produce PCDD/PCDF as an unwanted byproduct. Higher emissions have been associated with the use of chlorinated scavengers in leaded gasoline. However, when unleaded gasoline is used and a catalytic converter is installed for the removal of NOx and unburned hydrocarbons, the emissions of PCDD/PCDF are negligible. The only release vector is to air. Other release vectors are not present.

### Emission Factors

PCDD/PCDF emission factors for four source classes are listed in Table II.5.3. Revised or newly added emission factors are highlighted in red. More detailed information on how these emission factors have been derived can be found in Annex 41.

### Guidance for classification of sources

**Class 1** includes all types of gasoline 4-stroke vehicles which are fueled with leaded (ethylated) gasoline (gasoline with a content of lead of more than 0.15/0.013 g/l).

**Class 2** includes all types of 4-stroke vehicles which are fueled with gasoline excluding ethylated gasoline or LPG, and are not equipped with catalyst or where the catalyst is not adequate or out of order. Euro class 1 vehicles and lower (or their equivalent in other countries) belong to this class.

**Class 3** includes all types of 4-stroke vehicles which are fueled with gasoline excluding ethylated gasoline, or LPG and equipped with proper catalyst. Euro class 2 vehicles and higher (and their equivalent in other countries) belong to this class.

**Class 4** includes all types of 4-stroke vehicles with catalyst which are powered by ethanol or fuel mix (gasoline-ethanol such as E85), where the share of ethanol is of more than 50%.

**Table II.5.3 PCDD/PCDF emission factors for source category 5a 4-Stroke Engines**

5a	4-Stroke Engines	Emission Factors (µg TEQ/t fuel burned)
----	------------------	---



Classification		Air	Water	Land	Product	Residue
1	Leaded fuel*	2.2	NA	NA	NA	NA
2	Unleaded gasoline without catalyst*	0.1	NA	NA	NA	NA
3	Unleaded gasoline with catalyst* (**)	0.001	NA	NA	NA	NA
4	Ethanol with catalyst	0.0007	NA	NA	NA	NA

\* If consumption data are given in liters (L), note that 1 L of gasoline has a mass of 0.74 kg; thus a conversion factor of 0.00074 must be used to convert liters into tons.

\*\* Emissions from engines with inadequate or out-of-order catalyst should be calculated using class 2 emission factor.

### Activity rates

Activity rates which characterize the transport sector may be assessed using:

- National statistics on motor fuels consumption, export-import, production (trade, customs etc.);
- National statistics on car fleet structure;
- National, regional, local databases on car registration with indication of their state and ecological characteristics;
- International statistics (Eurostat, IEA).

Activity rates necessary for compiling the PCDD/PCDF emission inventory for the transportation sector (*i.e.* fuel used (sold) and vehicle fleet characteristics) are generally found in two independent data sources. Therefore, in some cases, it is not easy to estimate fuel consumption according to the type of vehicle. Additional research will be necessary. The example inventory 6 shows some models that may be used in such cases.

### Level of confidence

The confidence in PCDD/PCDF emission factors for this source category depends on the source class. Taking into account the levels of PCDD/PCDF concentrations in emissions and their variation according to the source class, a medium confidence level is assigned to class 2 and class 3 emission factors, a high confidence level to class 1 emission factor, and a low confidence level to class 4 emission factor.

## 5b 2-Stroke Engines

Most small gasoline powered internal combustion engines used today in boats, jet-skis, mopeds, small motorcycles, tuk-tuks, lawnmowers, chain saws, and other vehicles are 2- stroke engines. These engines follow the same thermodynamic combustion cycle as the 4-stroke engines, but are limited to 2 strokes: the combined exhaust and intake stroke, and the compression, ignition and combustion stroke. All these strokes occur during only one full revolution of the crankshaft. Lubrication is usually by oil added with the fuel. Therefore, higher amounts of pollutants may be released and the efficiency may be lower than 4-stroke engines. The only release vector is to the air. All other release vectors are not present.

## Emission Factors

PCDD/PCDF emission factors for two source classes are listed in Table II.5.4. Detailed information on how these emission factors have been derived can be found in Annex 42.

### Guidance for classification of sources

**Class 1** includes all mobile machinery (mopeds, small motorcycles, tuk-tuks, boats, jet-skis, lawnmowers, chain saws and other) with 2-stroke engines fueled by leaded fuel (with lead content more than 0.15/0.013 g/l).

**Class 2** includes all mobile machinery (mopeds, small motorcycles, tuk-tuks, boats, jet-skis, lawnmowers, chain saws, and other) with 2-stroke engines fueled by unleaded fuel (with lead content less than 0.15/0.013 g/l).

**Table II.5.4 PCDD/PCDF emission factors for source category 5b 2-Stroke Engines**

5b	2-Stroke Engines	Emission Factors ( $\mu\text{g TEQ/t fuel burned}$ )				
		Air	Water	Land	Product	Residue
	<b>Classification</b>					
1	Leaded fuel*	3.5	NA	NA	NA	NA
2	Unleaded fuel *	2.5	NA	NA	NA	NA

\* if consumption data are given in liters (L), note that 1 L of gasoline has a mass of 0.74 kg; thus a conversion factor of 0.00074 must be used to convert liters into tons

### Activity rates

Activity rates which characterize the transport sector may be assessed using:

- National statistics on motor fuels consumption, export-import, production (trade, customs etc.);
- National statistics on car fleet structure;
- National, regional, local databases on car registration with indication of their state and ecological characteristics;
- International statistics (Eurostat, IEA).

Activity rates necessary for compiling the PCDD/PCDF emission inventory for the transportation sector (*i.e.* fuel used (sold) and vehicle fleet characteristics) are generally found in two independent data sources. Therefore, in some cases, it is not easy to estimate fuel consumption according to the type of vehicle. Additional research will be necessary. The example inventory 6 shows some models that may be used in such cases.

### Level of confidence

PCDD/PCDF emission measurements from this source category are limited; taking into account the heterogeneity of this source group, a low level of confidence is assigned to these emission factors.

## 5c Diesel Engines

Diesel engines are used in heavy trucks, light trucks, passenger cars, locomotives, heavy construction equipment, boats, Diesel generators, pumps, and farm equipment including tractors and other large equipment. These engines use Diesel (light oil) and a 4-stroke cycle. Compression is used for ignition rather than a spark. Air is taken into the cylinder and compressed. Diesel fuel is added at high

pressure and burned, resulting in a more efficient use of fuel and lower emissions. Unfortunately, particle emissions in form of soot are also associated with the operation of Diesel engines, due to incomplete combustion especially during the start-up, warming and load changes. Deposition of this soot can lead to releases via residues. Particulate emissions from Diesel engines are well known to contain high concentrations of polycyclic aromatic hydrocarbons (PAH). However, data on PCDD/PCDF concentrations in Diesel soot are not available. As for other unintentional POPs, no data or almost zero emission for recent diesel engines with after-treatment of emissions have been reported (Laroo *et al.* 2011).

### Emission Factors

PCDD/PCDF emission factors for two source classes are listed in Table II.5.5. Revised or newly added emission factors are highlighted in red. Detailed information on how these emission factors have been derived can be found in Annex 43.

### Guidance for classification of sources

**Class 1** includes all mobile machinery (heavy trucks, light trucks, passenger cars, locomotives, heavy construction equipment, boats, Diesel generators, pumps, farm equipment etc.) fueled with regular Diesel.

**Class 2** includes Diesel vehicles (heavy duty, passenger cars etc.) fueled with Diesel including 20% or more biofuel.

**Table II.5.5 PCDD/PCDF emission factors for source category 5c Diesel Engines**

5c	Diesel Engines	Emission Factors ( $\mu\text{g TEQ/t diesel}$ )				
		Air	Water	Land	Product	Residue
1	Regular Diesel*	0.1	NA	NA	NA	ND
2	Biodiesel	<b>0.07</b>	NA	NA	NA	ND

\* if consumption data are given in liters (L), note that 1 L of Diesel has a mass of 0.83-0.86 (depending on brand of Diesel); thus appropriate conversion factor (in the range 0.00083-0.00086) must be used to convert liters into tons

### Activity rates

Activity rates which characterize the transport sector may be assessed using:

- National statistics on motor fuels consumption, export-import, production (trade, customs etc.);
- National statistics on car fleet structure;
- National, regional, local databases on car registration with indication of their state and ecological characteristics;
- International statistics (Eurostat, IEA).

Activity rates necessary for compiling the PCDD/PCDF emission inventory for the transportation sector (*i.e.* fuel used (sold) and vehicle fleet characteristics) are generally found in two independent data sources. Therefore, in some cases, it is not easy to estimate fuel consumption according to the type of vehicle. Additional research will be necessary. The example inventory 6 shows some models that may be used in such cases.

### Level of confidence

PCDD/PCDF emission measurements from regular diesel engines are limited, taking into account the large number of vehicles; also, emission may vary widely according to the engine technology, mileage and maintenance conditions. A medium level of confidence is assigned to class 1 emission factor. Furthermore, the use of biodiesel is more recent and emission data are also limited. Thus, a low/medium level of confidence is assigned to class 2 emission factor.

## 5d Heavy Oil Fired Engines

Heavy fuel oil (HFO) fired engines are used for ships, tanks, stationary power generators, and some other large quasi-stationary motors. The availability of emission factors is very limited and presently no distinction can be made with respect to the composition of the fuels, chlorine content, type of catalytic metals present, etc.

### Emission Factors

PCDD/PCDF emission factors for one source class are listed in Table II.5.6. Revised or newly added emission factors are highlighted in red. Emission factors for other unintentional POPs (HCB and PCB) were also derived based on Cooper (2005) and are listed in Annex 44. Detailed information on how default emission factors have been derived can also be found in Annex 44.

**Table II.5.6 PCDD/PCDF emission factors for source category 5d Heavy Oil Fired Engines**

5d	Heavy Oil Fired Engines	Emission Factors ( $\mu\text{g TEQ/t fuel burned}$ )				
		Air	Water	Land	Product	Residue
1	All types	2	NA	NA	NA	ND

### Activity rates

Activity rates which characterize the transport sector may be assessed using:

- National statistics on motor fuels consumption, export-import, production (trade, customs etc.);
- National statistics on car fleet structure;
- National, regional, local databases on car registration with indication of their state and ecological characteristics;
- International statistics (Eurostat, IEA).

Activity rates necessary for compiling the PCDD/PCDF emission inventory for the transportation sector (*i.e.* fuel used (sold) and vehicle fleet characteristics) are generally found in two independent data sources. Therefore, in some cases, it is not easy to estimate fuel consumption according to the type of vehicle. Additional research will be necessary. The example inventory 6 shows some models that may be used in such cases.

### Level of confidence

PCDD/PCDF emission measurements from this source category are limited, taking into account the large number of vehicles, technology, fuel variability, age and maintenance conditions. PCDD/PCDF emission factors are thus provided with medium confidence.

## 6 – Open Burning Processes

This source group comprises two source categories of open burning (*i.e.*, combustion with no equipment or containment present) of the following materials, as indicated in Table II.6.1:

- Biomass (forests, savannahs, grasslands, agricultural crop residues, including sugarcane), and
- Waste (mainly domestic or municipal solid waste burned in official landfills, other dumps or private backyards; vehicles, buildings and factories burned in accidental fires; and construction/demolition waste).

None of these combustion processes and fires occurs under defined or optimized conditions. Aeration occurs by natural ventilation. In the first source category, burning conditions vary from poor to highly efficient depending on the type of fuel, fuel arrangement and the ambient conditions such as humidity, temperature, fuel moisture and wind speed. In the second group, burning conditions are commonly poor due to heterogeneous composition, compacted and poorly mixed fuel materials. Further, moisture and lack of oxygen may contribute to additional complexity. Typically, there is no intervention to select the fuels or to improve the combustion conditions. In certain jurisdictions, some of these processes are not authorized and are therefore un-documented. Consequently the releases from these processes tend to be underestimated because of difficulties in assessing the overall national activity.

Throughout this source group, releases of unintentional POPs with solid residues such as combustion ashes are regarded as releases to land rather than release to residue, since due to the lack of containment, the ashes are disposed on land and are typically not collected for further disposal. Therefore, an  $EF_{Land}$  is provided. Subsequently, to avoid double-counting, no  $EF_{Residue}$  is provided, although the release vector is ash.

This Toolkit differentiates between two major source categories (Table II.6.1):

**Table II.6.1 Overview of source categories included in group 6 - Open Burning Processes**

6 – Open Burning Processes		Potential release route				
		Air	Water	Land	Product	Residue
a	Biomass burning	X	(x)	X		(x)
b	Waste burning and accidental fires	X	(x)	X		(X)

With relevance to the provisions of Article 5, sources in this category are listed in Annex C as follows:

**Table II.6.2 Relevance to Article 5, Annex C of the Stockholm Convention**

No	Toolkit source category	Part II	Part III	Relevant source category in Annex C
6b	Waste burning and accidental fires		X	Open burning of waste including burning of landfills

An example of elaborating source inventory and release estimate for this source group is included in the example inventory 7.

## 6a Biomass Burning

This category covers the burning of biomass where it occurs in the open. It includes all fires in natural and managed ecosystems including forests, woodlands, shrublands, grasslands, savannah, plantations, and all fires in agricultural lands. This section does not address any process that converts biomass into another form of energy such as steam, controlled combustion in appliances such as stoves, furnaces and boilers. Such processes are covered in Group 3 - Power Generation and Heating.

Fires in natural and managed ecosystems include wildfires regardless of the ignition source and all fires conducted for land management including fuel reduction for wildfire mitigation, biodiversity management, forest slash removal and seed bed preparation following logging operation, and the removal of forest biomass following land clearing for conversion to agriculture and other land uses. Ignition sources include lightning, deliberate arson, accidental ignitions (*e.g.*, burning cigarettes, glass, welders, power transmission lines) and authorized ignitions for management purposes. A broad definition of forest class is applied in the Toolkit. It includes temperate and tropical rainforests; temperate, boreal, and Eucalyptus forests; temperate shrublands; tundra; peatlands; and forest plantations.

Savannah woodlands and savannah grasslands are ecosystems comprising open and sparse woodlands dominated by an extensive understory of grasses. The annual climate is a short productive wet season followed by a long drought during which the grasses senesce and the fuels dry. Fire is an essential and integral component of these ecosystems and has been traditionally used by indigenous populations for many millennia to manage animal and plant food sources (Russell-Smith *et al.* 2009a). Fire return interval in these regions is short, typically less than three years (Archibald *et al.* 2010). Fires in these ecosystems comprise the major proportion of global annual fire affected land area (Gilio *et al.* 2006).

Fires are also commonly used in agriculture. Post-harvest field burning is practiced to remove residues prior to soil preparation and sowing, to control weeds, and release nutrients for the next crop cycle, however, also negative effects on soil may occur and, ideally, this practice is used judiciously. It is applied extensively, but not exclusively, in cereal production (wheat, rice, maize, and coarse grains) in many regions. Pre-harvest burning is used in some crops, particularly sugar cane, to remove debris and pests and to facilitate manual and mechanical harvesting.

### Emission Factors

Emission from this source category will vary depending on ambient atmospheric conditions, fuel type and structure, composition, and contamination with PCDD/PCDF precursors. When biomass fuels are wet or compacted, burning efficiency is poor, combustion temperature is low, and consequently, PCDD/PCDF emissions are high. PCDD/PCDF emissions are also assumed to be high when the biomass has been treated with pesticides that act as PCDD/PCDF precursors or as catalysts for PCDD/PCDF formation, in these cases the biomass is said to be “impacted”. At the other extreme, burning of dry, virgin biomass of small size would burn efficiently and have small emission factors.

Emission factors for PCDD/PCDF are listed in Table II.6.3, and for dioxin-like PCB are listed in Table III.45.1 in Annex 45. Detailed information on the derivation of default emission factors can also be found in Annex 45. Revised or newly added PCDD/PCDF emission factors are highlighted in red.

### Guidance for classification of sources

**Class 1** includes the open burning of agricultural biomass in the field under conditions that may favor increased PCDD/PCDF formation and release. Although little experimental data exist, it is assumed that prior application of chlorinated pesticides to crops would increase PCDD/PCDF formation and release. Other contributing factors include unfavorable burning conditions such as large piles or humid materials. In general, the biomass may be cereal, legume oilseed or fibre crops and can be burned as stubble, cut and left in the field or bundled into piles. This class potentially includes a wide range of fire intensity from relatively cool, low-intensity fires with mostly smouldering combustion to hot, high intensity, fast-moving fires with efficient combustion.

**Class 2** addresses the same type of biomass and geometry of the fuel; however, the fuel and the burning conditions would constitute best environmental practices such as the absence of precursors or other conditions that favor PCDD/PCDF formation. These fires also range from cool to hot fires.

**Class 3** addresses the pre-harvest burning of sugarcane in the field. It is assumed that the leaves will be burned off and the stems will remain in the field for harvest either manually or by machine. These fires are usually intense, fast moving and of relatively short duration.

**Class 4** includes all types of forest fires, including those in which whole trees are burned, canopy fires and forest litter burns.

**Class 5** addresses fires in savannahs and grasslands. Fires in savannahs frequently consume low shrubs in addition to grass and litter from trees.

**Table II.6.3 PCDD/PCDF emission factors for source category 6a Biomass Burning**

6a	Biomass Burning Classification	Emission Factors (µg TEQ/t material burned)				
		Air	Water	Land	Product	Residue
1	Agricultural residue burning in the field, impacted, poor burning conditions	30	ND	10	NA	NA
2	Agricultural residue burning in the field, not impacted	0.5	ND	0.05	NA	NA
3	Sugarcane burning	4	ND	0.05	NA	NA
4	Forest fires	1	ND	0.15	NA	NA
5	Grassland and savannah fires	0.5	ND	0.15	NA	NA

### Activity rates

The activity for this source category is the mass of fuel consumed as tons dry matter. National data are not available in this form, and therefore the activity is calculated using other information, such as the total area in each emission class multiplied by the density of combustible fuel (*e.g.*, tons dry matter consumed per hectare burned). Combustible fuel density is determined from measurements of above ground biomass of potential fuel classes and the fraction of this mass that is actually burned. Consequently combustible fuel density varies with vegetation class, fire class and season. A compilation of average fuel densities for most vegetation classes relevant to the Toolkit classes is provided in Table II.6.4.

The best source of information on where fires occur in a country may be fire departments. Departments and research institutions for agriculture and forest may be the best sources for the estimation of biomass grown in a given region.

Some of these data are collated into international databases, *e.g.*, FAO agricultural statistics which can provide an alternative source of activity data in the absence of readily available local sources. There are also published international compilations of fire-affected area derived from remote sensing as both regional summaries and detailed spatial statistics (Van der Werf *et al.* 2006). These sources can be valuable supplements to national statistics and are useful for QA/QC assessment of inventory emission estimates.

For orientation, the information on burning efficiency for natural ecosystems such as forests and major crops in agriculture is presented in Table II.6.4. This table also gives advice as to the type of fire.

**Table II.6.4 Summary of information on biomass fuel consumed in open fires (adapted from IPPC 2006)**

<b>Ecosystem</b>	<b>Class</b>	<b>Fire category</b>	<b>Fuel burned (t dm/ha)</b>
<b>Natural Ecosystems</b>			
Tropical Forest	Primary		43
	Secondary		23
	Tertiary		32
Boreal		Wildfire	21
		Surface fire	3.2
		Post logging slash	23
		Land clearing	52
Eucalyptus		Wildfire	33
		Prescribed fire	10
		Post logging slash	115
		Land clearing	78
Other temperate forest		Wildfire	11
		Post logging slash	48
		Land clearing	25
Shrublands			10
Tropical savannahs	Woodland	Early dry season	2.8
	Woodland	Late dry season	4.2
Other savannah	Woodlands	Early dry season	0.6
	Woodlands	Late dry season	2.4
Savannah grasslands	Tropical/Subtropical	Early dry season	1.6
	Tropical/Subtropical	Late dry season	4.8
	Grassland	Late dry season	3.5
	Tropical Pasture	Late dry season	8.3
Other natural ecosystems	Peatland		21
	Tundra		5
<b>Agricultural Systems</b>			
Wheat			3.6



Maize	8
Rice	4.4
Sugarcane	5.2

Compiled from IPCC 2006 (Volume 4, Chapter 2, Tables 2.4 and 2.5) and Russell-Smith *et al.* 2009b.

Table II.6.4 should be supplemented with country-specific data where available. Some examples of the amount of material expected to be involved in a biomass fire based on the land area involved are shown below.

In the UK, values were derived as follows:

- Heather moorland – material consumed in fires – 8 tons per hectare.
- UK forest – material consumed in fire – 23 tons per hectare.

For estimating the releases of PCDD/PCDF from biomass fires, countries may wish to apply the approach as shown for France – and adjust the numbers according to their climatic conditions and vegetation. In the French inventory, the following approaches have been used to estimate the PCDD/PCDF releases from forest fires (Béguier 2004):

- Forests/vegetation has been classified according to climatic zones resulting in temperate and Mediterranean (south of France) zones;
- In the temperate zone, forests typically have 20 kg of biomass per square meter (20 kg/m<sup>2</sup>) corresponding to 200 t/ha. In the Mediterranean zone, the biomass is 4 kg/m<sup>2</sup> or 40 t/ha;
- In the temperate zone on average, 20% of the vegetation is removed by the fires hence the fuel burned is 40 t/ha. In the Mediterranean zone, the fires are more efficient with an average of 25% above ground biomass removed; thus, the fires in southern France will generate PCDD/PCDF from 10 t of biomass per hectare affected by the fire.

The Philippines report that on average 43 t/ha is consumed in forest fires in their region.

Fuel loads for crops can be estimated from crop production data that are regularly collected and reported by agricultural companies and agencies. For pre-harvest burning of sugar cane, the following approximation to estimate the amount of biomass burned can be used: about 300 kg of biomass is burned for each ton of sugar produced (Choong Kwet Yive 2004).

For post-harvest burning, Southeast Asian countries used the following approximation to estimate the mass of rice straw burned: harvest residues of 25% w/w are being generated from rice. In other words: 250 kg of rice straw are generated per ton of (polished) rice produced.

### Level of Confidence

6a	Biomass Burning	Level of Confidence	
	Classification		
1	Agricultural residue burning in the field, impacted poor burning conditions	Medium	Value is extrapolated from common knowledge the processes
2	Agricultural residue burning in the field, <i>e.g.</i> , cereal crops, not impacted	High	Relatively large number of consistent results in narrow range, relatively wide geographic coverage

3	Sugarcane burning	Medium	Relatively many consistent results published in peer-reviewed literature, largest range of results within this sub-category, limited geographic range
4	Forest fires	High	Relatively large number of consistent results in narrow range, relatively wide geographic coverage
5	Grassland and savannah fires	Medium	Limited number of very consistent results, small range of results

## 6b Open Burning of Waste and Accidental Fires

This source category includes the deliberate combustion of waste materials for disposal where no furnace or similar is used – for example the burning of domestic waste and other waste in piles in the open, the burning of waste in dumps – both deliberate or accidental, and fires in buildings, cars and other vehicles. In this source category, there is no recovery of the calorific content of the fuel.

As with the source classes under category 6a, releases of unintentional POPs in solid residues such as combustion ashes are regarded as releases to land rather than release to residue since the ashes are disposed on land and are typically not collected for further disposal. Therefore, to avoid double-counting, an  $EF_{Land}$  is provided instead of an  $EF_{Residue}$ .

### Emission Factors

Emission factors for PCDD/PCDF are available for five classes as shown in Table II.6.5. Revised or newly added emission factors are highlighted in red. For dioxin-like PCB, available emission factors are listed in Table III.46.1 in Annex 46. Detailed information on how default emission factors have been derived can also be found in Annex 46, along with detailed guidance on activity rates.

### Guidance for classification of sources

**Class 1** refers to spontaneous or intentional fires occurring in a municipal or domestic waste repository. Waste at such sites may often include refuse from offices, small factories or workshops and restaurants. In some cases, these fires have the purpose of reducing the volume of waste in the repository. Typically, the waste will be relatively high in organic carbon. The combustible material will tend to be compacted and moist, and will burn poorly and slowly; hence the higher emission factor than for class 3. Typically, ignition occurs from either sparks occurring at the surface area, from self-ignition inside the waste body or intentionally for management reasons. It should be noted that fires of this type are very uncommon in modern engineered landfills, particularly those with compaction, daily soil cover, runoff water recycling or leachate and landfill gas collection.

**Class 2** includes accidental fires involving buildings, such as homes and factories. Consequently, emission factors must be given per event and they depend strongly on the materials burned and on the nature of the fire. There is limited information on releases from these fires and a single indicative figure is given to cover all accidental fires excluding fires in vehicles. Chemical fires may lead to very high releases where certain precursor chemicals are involved. However there is insufficient information to assess releases from chemical fires as a distinct category so releases are included in

this class of accidental fires. It should be noted that specific incidents may give rise to local contamination and potential “hot spots”.

**Class 3** includes burning of domestic waste in open piles, pits, barrels, with no pollution controls. The waste is typically characterized by a large fraction of organic/agricultural waste and is loosely arranged (not compacted).

**Class 4** includes fires that involve cars and other vehicles. Limited data are available for deriving emission factors for such events and vehicles involved can vary considerably so emissions are expected to vary as well. Consequently the emission factors here are for rough estimates only.

**Class 5** includes open burning of wood and other materials used in construction and remaining after demolition. Such wood may be painted or treated with preservatives and plastics, including PVC, or may be present in the other materials burned.

**Table II.6.5 PCDD/PCDF emission factors for source category 6b Open Burning of Waste and Accidental Fires**

6b	Open Burning of Waste and Accidental Fires	Emission Factors (µg TEQ/t material burned)				
		Air	Water	Land	Product	Residue
1	Fires at waste dumps (compacted, wet, high organic carbon content)	300	ND	10*	NA	NA
2	Accidental fires in houses, factories	400	ND	400	NA	NA
3	Open burning of domestic waste	40	ND	1*	NA	NA
4	Accidental fires in vehicles (µg TEQ per vehicle)	100	ND	18	NA	NA
5	Open burning of wood (construction/demolition)	60	10	10	NA	NA

\* Based on a few field measurements and consistent with the biomass burn  $EF_{Land}$  where the release in the ashes is 5%-10% of the  $EF_{Air}$ .

### Level of Confidence

Through recent studies, more data have been generated including results from developing countries, targeted to generate emission factors which are closer to real country situations. These studies and results cover a larger geographic area than before, and have been published in peer-reviewed literature. On the other hand, extrapolation still needs to be done to estimate the activity and the processes, which especially for source category 6b are not stable. Therefore, although the studies are of good scientific quality, the results are scattered due to heterogeneity of the processes, fuels, and other variables.

A new practical approach has been developed to allow inventory developers to better characterize the activity rate, *i.e.*, estimate the mass of waste that is burned in the open air. The new method is presented in Annex 46.

6b	Open Burning of Waste and Accidental Fires	Level of Confidence
	Classification	

1	Fires at waste dumps (compacted, wet, high C <sub>org</sub> content)	Medium	Few studies, consistently large range of results, published in peer-review literature
2	Accidental fires in houses, factories	Low	Very few results, large range of data; process is not stable
3	Open burning of domestic waste	Medium	Few studies, consistently large range of results, relatively large geographic area, published in peer-review literature
4	Accidental fires in vehicles (µg TEQ per vehicle)	Low	Very few studies with consistent data; process is not stable
5	Open burning of wood (construction/demolition)	Low	Value is extrapolated from common knowledge the processes

## 7 – Production and Use of Chemicals and Consumer Goods

This source group addresses chemicals and consumer goods that are associated with potential formation and release of PCDD/PCDF during their production and/or use. PCDD/PCDF formation takes place only in processes that involve some form of chlorine. However, PCDD/PCDF may be found in other processes in which PCDD/PCDF-contaminated feedstocks and raw materials are used. While no global assessment is available, the production of chemicals is estimated to account for 34% of total PCDD/PCDF releases in the European Union, with a strong decreasing trend (BiPRO 2005).

Detailed descriptions of the production processes of some chemicals and consumer goods can be found in the BAT&BEP Guidelines, in particular, Section VI.F. – Specific Chemical Production Processes Releasing Chemicals Listed in Annex C, Section V.C - Production of Pulp Using Elemental Chlorine or Chemicals Generating Elemental Chlorine, and Section VI.J – Textile and Leather Dyeing (with Chloranil) and Finishing (with Alkaline Extraction).

In addition to the chemicals addressed in Source Group 7, other chemicals and consumer goods have been reported to contain PCDD/PCDF or to release PCDD/PCDF to air, water or residues from their production processes and/or their use. Information on these sources that are not addressed in Source Group 7 can be found in Annex 2 Guidance on Identifying Sources of PCDD/PCDF.

As shown in Table II.7.1, the production and use of chemicals and consumer goods is divided into eight source categories that have the potential for PCDD/PCDF releases to air, water, land, residues, and products.

**Table II.7.1 Overview of source categories included in group 7 - Production and Use of Chemicals and Consumer Goods**

7 - Production and use of Chemicals and Consumer Goods		Potential release route				
		Air	Water	Land	Product	Residue
7a	Pulp and Paper Production	x	x		x	x
7b	Chlorinated Inorganic Chemicals	x	X		X	X
7c	Chlorinated Aliphatic Chemicals	x	X	(x)	X	X
7d	Chlorinated Aromatic Chemicals	x	X	(x)	X	X
7e	Other Chlorinated and Non-Chlorinated Chemicals	x	X	(x)	X	X
7f	Petroleum Production	x				x
7g	Textile Production		x		x	x
7h	Leather Refining		x		x	x

With relevance to the provisions of Article 5, sources in this category can be classified as follows:

**Table II.7.2. Relevance to Article 5, Annex C of the Stockholm Convention**

No	Toolkit source category	Part II	Part III	Relevant source category in Annex C

7a	Pulp and Paper Production	X		Production of pulp using elemental chlorine or chemicals generating elemental chlorine for bleaching
7b	Chlorinated Inorganic Chemicals		X	Specific chemical production processes releasing unintentionally formed persistent organic pollutants, especially production of chlorophenols and chloranil
7c	Chlorinated Aliphatic Chemicals		X	Specific chemical production processes releasing unintentionally formed persistent organic pollutants, especially production of chlorophenols and chloranil
7d	Chlorinated Aromatic Chemicals		X	Specific chemical production processes releasing unintentionally formed persistent organic pollutants, especially production of chlorophenols and chloranil
7e	Other Chlorinated and Non-Chlorinated Chemicals		X	Specific chemical production processes releasing unintentionally formed persistent organic pollutants, especially production of chlorophenols and chloranil
7g	Textile production		X	Textile and leather dyeing (with chloranil) and finishing (with alkaline extraction)
7h	Leather refining		X	Textile and leather dyeing (with chloranil) and finishing (with alkaline extraction)

An example of elaborating source inventory and release estimate for this source group is included in the example inventory 8.

### Activity Rates

In general, activity rates for source categories, classes and sub-classes in Source Group 7 can be determined by consulting sources such as the following:

- National , regional and global statistics on production and use of consumer goods and chemicals, including pesticides and pesticide use;
- Research consortia such as CMAI and SRI Consulting, <http://chemical.ihs.com/>, ICIS Chemical Business, <http://www.icis.com/>, and Nexant, <http://www.chemsystems.com/>, that compile comprehensive reports on production and producers of chemicals and consumer goods at global, regional and national levels;

- National, regional and global associations of manufacturers and users of chemicals and consumer goods;
- Industrial trade journals and magazines; and
- Questionnaires to chemical and consumer goods production facilities.

An alternative method for determining production rates that uses nameplate capacity and Capacity Utilization Factor (CUF) is found in Chapter 2.3.

## **7a Pulp and Paper Production**

Feedstocks for pulp production include wood as well as non-wood materials such as wheat straws, reed, and bamboo. The major types of pulp and paper mills are as follows (EC 2001):

- Kraft or sulfate pulp and paper mills account for about 80% of world pulp production;
- Sulfite pulp and paper mills account for about 10% of world production;
- Mechanical pulp and paper mills; and
- Recycled fiber paper mills.

Pulp and paper production processes may release PCDD/PCDF to these vectors:

- Releases to air from energy generation<sup>9</sup>;
- Releases to water in wastewater treatment effluents;
- Releases to residue as wastewater treatment sludge and ashes or smelt; and
- Releases to product – pulp and paper.

In general terms, the process of making paper and paperboard consists of three steps: pulp making, pulp processing, and paper/paperboard making. A detailed description of the process is available in the BAT&BEP Guidelines.

### **Emission Factors**

PCDD/PCDF emission factors for on-site heat/power production are listed in Table II.7.3 and those for other pulp and paper production processes are presented according to the activity type in Tables II.7.4 and II.7.5. Revised or newly added emission factors are highlighted in red. Detailed information on the derivation of emission factors can be found in Annex 47.

### **Guidance for classification of sources**

On-site boilers for heat/power generation for the pulp and paper production are classified as follows:

**Class 1** Recovery boilers fired with black liquor or black liquor/bio-sludge (for sludge for modern bleaching technology)<sup>10</sup>;

**Class 2** Power boilers fired with sludge and biomass/bark;

**Class 3** Power boilers fired with salt-laden wood.

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<sup>9</sup> From lime kilns (see source group 4), smelt dissolving tanks at Kraft mills, and from any on-site incinerators for disposing of sludge and other wastes not used as fuels for power or auxiliary boilers.

<sup>10</sup> In some pulp mills, bio-sludge is mixed with black liquor and burned in the recovery boiler at a very low proportion (La Fond *et al.* 1997, Van Heiningen and Blackwell 1995).

Processes for producing pulp and paper are placed in the following classes:

**Class 1** facilities use the Kraft process for pulping non-wood fibers that are potentially contaminated with PCP and bleach with Cl<sub>2</sub>.

**Class 2** facilities use the Kraft process for pulping fibers that are PCP-free and bleach with Cl<sub>2</sub>.

**Class 3** facilities use the Kraft process for pulping and bleach first with Cl<sub>2</sub>, followed by non-chlorine bleaching technologies.

**Class 4** facilities use the sulfite process for pulping and bleach with Cl<sub>2</sub>.

**Class 5** facilities use the Kraft process for pulping and bleach with chlorine dioxide (ClO<sub>2</sub>).

**Class 6** facilities use the sulfite process for pulping and bleach with ClO<sub>2</sub> or with totally chlorine-free (TCF) technologies.

**Class 7** facilities use thermo-chemical processes to produce pulp and bleach via lignin-saving methods that use sodium dithionite (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>), peroxide (H<sub>2</sub>O<sub>2</sub>) or a mixture of these two chemicals.

**Class 8** facilities are those engaged in recycling paper from contaminated waste paper – paper that is made from pulp produced by Class 1 through Class 4 facilities.

**Class 9** facilities are those engaged in recycling paper from modern paper – paper derived from pulp produced by Class 5 and Class 7 facilities.

To assist in estimating PCDD/PCDF releases, typical PCDD/PCDF values are given in terms of tons of air-dried pulp and paper produced (ADt), with pulp at 90% dryness and paper as the finished paper, which typically has 94-96% dryness. Typical PCDD/PCDF concentrations in effluent, residues and products are also presented for use when mass production data are not available. Emission factors for all wood fiber mills (classes 2-7) are based on the assumption that all such mills have wastewater treatment facilities that produce sludge and effluent low in suspended solids.

**Table II.7.3 PCDD/PCDF emission factors for source category 7a Power Boilers in the Pulp and Paper Industry**

7a	Pulp and Paper Production	EF <sub>Air</sub> µg TEQ/ADt <sup>A</sup>	EF <sub>Residue</sub> µg TEQ/t ash <sup>B</sup>
<b>Classification</b>			
1	Recovery boilers fueled with black liquor	0.03	ND
2	Power boilers fueled with sludge and/or biomass/bark	0.5	5
3	Power boilers fueled with salt-laden wood	13	228

<sup>A</sup> Air-Dried tons

<sup>B</sup> Bottom ash or bottom ash plus fly ash

**Table II.7.4 PCDD/PCDF emission factors for source category 7a Wastewater Effluent from Pulp and Paper Production and Pulp Sludges**

7a	Pulp and Paper Production	EF <sub>Water</sub> Wastewater effluent		EF <sub>Residue</sub> Sludge	
		µg TEQ/ ADt pulp	µg TEQ/L	µg TEQ/ ADt pulp	µg TEQ/t Sludge
<b>Classification</b>					



1	Kraft process, Cl <sub>2</sub> , non-wood, PCP-contaminated fibers	ND	300*	ND	ND
2	Kraft process, Cl <sub>2</sub>	4.5	70	4.5	100
3	Mixed technology (Cl <sub>2</sub> partially in 1st step, followed by non-chlorine bleaching)	1.0	15	1.5	30
4	Sulfite process, Cl <sub>2</sub>	ND	ND	ND	ND
5	Kraft process, ClO <sub>2</sub>	0.06	2	0.2	10
6	Sulfite process, either ClO <sub>2</sub> or totally chlorine-free (TCF)	ND	ND	ND	ND
7	Thermo-mechanical process, lignin-saving chemical treatment	ND	ND	ND	ND
8	Paper recycling with contaminated waste paper	ND	30**	ND	ND
9	Paper recycling with modern paper	ND	ND	ND	ND

\* Raw effluent

\*\* Wastewater from deinking system

**Table II.7.5 PCDD/PCDF emission factors for source category 7a Pulp and Paper Products**

7a	Pulp and Paper Production	EF <sub>Product</sub> µg TEQ/t product
<b>Classification</b>		
1	Kraft process, Cl <sub>2</sub> , non-wood, PCP-contaminated fibers	30
2	Kraft process, Cl <sub>2</sub>	10
3	Mixed technology (Cl <sub>2</sub> partially in 1st step, followed by non-chlorine bleaching)	3
4	Sulfite process, Cl <sub>2</sub>	1
5	Kraft process, ClO <sub>2</sub>	0.5
6	Sulfite process, either ClO <sub>2</sub> or totally chlorine-free (TCF)	0.1
7	Thermo-mechanical process, lignin-saving chemical treatment	1
8	Recycling paper from contaminated waste paper	10
9	Recycling paper from modern paper	3

### Level of confidence

Emission factors for this source category are associated with a medium level of confidence for all classes, as they are based on a few reported data from a limited number of experiments with a limited geographical coverage, but not requiring expert judgment.

## 7b Chlorinated Inorganic Chemicals

For groups 7b through 7h, the following definitions of classes should be applied:

### Guidance for classification of sources

**Low-end technologies:** No information available, or processes (reactions, purification steps and wastewater and waste treatment) are not controlled in respect to the formation of PCDD/PCDF or

other unintentional POPs. Chemical feedstocks, air emissions, wastewater, residues and products are not monitored for PCDD/PCDF, other unintentional POPs or indicator substances.

**Mid-range technologies:** Processes (reactions and purifications steps including prevention by process- and production-integrated measures and wastewater and waste treatment) are controlled to some extent to limit releases. Parameters of these processes (*e.g.* feedstock; temperature; presence or use of chlorine in some form and, if, used, its concentration) are also controlled to reduce formation and release of unintentional POPs. Process inputs and emissions to air, wastewater, residues and products are monitored to some extent for PCDD/PCDF, other unintentional POPs or indicator substances.

**High-end technologies:** Processes (reactions and purifications steps including prevention by process- and production-integrated measures and wastewater and waste treatment) are optimized for low or no releases. Parameters of these processes (*e.g.* feedstock; temperature; presence or use of chlorine in some form and, if, used, its concentration) are optimized for minimum formation and release of unintentional POPs. Chemicals, products or by-products, emissions to air, wastewater and residues are monitored for PCDD/PCDF, other unintentional POPs or indicator substances. A refining step is used where appropriate to minimize unintentional POPs in the final chemical, product or by-product. Process residues should be handled in an environmentally sound manner, as described in the guidance on the BAT and BEP.

### **Elemental Chlorine (Cl<sub>2</sub>)**

Production of Cl<sub>2</sub> (CAS 7782-50-5) is the first step in producing chemicals and consumer goods that contain chlorine, as well as those for which some form of chlorine is used during their production. Global production of Cl<sub>2</sub> was estimated to be 81.2 million tons per year in 2012 (CMAI 2011a) and its uses, on a worldwide basis, are as follows (Beal and Linak 2011):

- Almost 35% is used in the EDC/VCM/PVC production chain – production of ethylene dichloride (EDC), which is used to make vinyl chloride (VCM) that is polymerized to produce polyvinyl chloride (PVC);
- 15% is used in the manufacture of isocyanates and propylene oxide, both of which are building blocks for polyurethane;
- 20% is used to produce other organic derivatives;
- 20% is used in the production of inorganic chemicals; and
- The remaining 10% is used in a variety of processes, such as water and wastewater treatment.

Uses of Cl<sub>2</sub> vary greatly by country and region. In the chlor-alkali process, Cl<sub>2</sub> and caustic soda [sodium hydroxide (NaOH)] are produced in a mass ratio of 1:1.1 by the electrolysis of brine (sodium chloride). Factors that can influence PCDD/PCDF formation and release in the chlor-alkali process include process design and direct contact of Cl<sub>2</sub> with reactive materials, such as graphite electrodes and certain seals, gaskets, lubricants, etc.

Electrodes made of graphite, a form of elemental carbon, which often included tar as binder pitch, were widely used until the 1970s when, in many countries, they were replaced by titanium electrodes. Due in part to their contribution to PCDD/PCDF formation and release, graphite electrodes are not considered Best Available Technique (BAT). Limited data show that far lower levels

of PCDF may also be formed when titanium electrodes are used, perhaps through reactions of elemental chlorine with reactive gaskets and seals (USEPA 2004).

More detailed descriptions of the three main chlor-alkali processes are presented in the BAT&BEP Guidelines.

### Emission Factors

Emission factors are derived for four classes of Cl<sub>2</sub> production via the chlor-alkali process: one class that uses graphite electrodes without regard for equipment and operational standards, and three classes that use titanium electrodes. Revised or newly added emission factors are highlighted in red.

**Table II.7.6 PCDD/PCDF emission factors for source category 7b Elemental Chlorine Production**

7a	Elemental chlorine (Cl <sub>2</sub> ) Classification	Emission Factors (µg TEQ/ECU <sup>*</sup> )				
		Air	Water	Land	Product	Residue
	1. Chlorine/chlor-alkali production using graphite electrodes	ND	ND	ND	ND	20,000 µg TEQ/t sludge 1,000 µg TEQ/ECU
	2. Chlorine/chlor-alkali production using titanium electrodes					
	2a Low-end technologies	ND	17	ND	ND	27
	2b Mid-range technologies	ND	1.7 120 pg TEQ/L	ND	ND	1.7
	2c High-end technologies	ND	0.002	ND	ND	0.3

<sup>\*</sup> Electrochemical unit (ECU) consists of 1 ton of chlorine and 1.1 tons of caustic soda (NaOH)

### Level of Confidence

Emission factors in this section are associated with a low level of confidence for all classes since they are based on a low data range with limited geographical coverage.

## 7c Chlorinated Aliphatic Chemicals

### Ethylene Dichloride (EDC), Vinyl Chloride Monomer (VCM) and Polyvinyl Chloride (PVC)

Approximately 35% of global production of elemental chlorine is consumed by the production of ethylene dichloride (EDC) (CAS 107-06-2), vinyl chloride monomer (VCM) (CAS 75-01-4) and polyvinyl chloride (PVC) (CAS 9002-86-2) (Beal and Linak 2011). EDC is used almost exclusively for producing VCM and VCM is used almost exclusively in the production of PVC resin (Nexant 2009). In 2009, worldwide production of PVC was estimated at 32.3 million tons per year (GBI 2011).

PVC is produced by two major pathways:

- The EDC/VCM/PVC production chain uses ethylene derived from petroleum or natural gas as its primary feedstock and accounts for about two-thirds of global PVC production; and
- The acetylene/VCM/PVC production chain which uses acetylene derived from coal as the primary feedstock and accounts for the remaining one-third of global PVC production (CMAI 2011b).

The EDC/VCM/PVC production chain consists of five major processes:

1. EDC production
  - a. Direct chlorination of ethylene using elemental chlorine in the presence of an iron catalyst; and/or
  - b. Oxychlorination of ethylene using hydrogen chloride (HCl) and air or oxygen in the presence of a copper catalyst;
2. Purification of EDC;
3. VCM production via thermal cracking of EDC, which also produces HCl that may be recycled into the oxychlorination process;
4. Purification of VCM; and
5. PVC production via polymerization of VCM.

Oxychlorination of ethylene to produce EDC has been described as the most favorable process step in the chemical industry for the formation of PCDD/PCDF (UNEP 2005). However, PCDD/PCDF are also known to occur in other processes in the EDC/VCM/PVC production chain (Weiss and Kandle 2006).

Within the EDC/VCM/PVC chain, most EDC production is a balanced mix of direct chlorination and oxychlorination, although some sites are direct chlorination only, or oversized for oxychlorination. Most EDC production is integrated with VCM production on the same site. However, some facilities produce only EDC and ship it elsewhere, and, perhaps more commonly, VCM production facilities ship their VCM elsewhere for polymerization into PVC. PCDD/PCDF can be released to one or more vectors from the production of EDC, VCM, and PVC, as detailed in Annex 48.

The acetylene/VCM/PVC production chain entails the following major processes:

1. VCM production via the reaction of acetylene with HCl in the presence of a mercuric chloride catalyst;
2. Purification of VCM; and
3. Polymerization of VCM to form PVC.

The acetylene/VCM/PVC production chain is largely used in China, where it accounts for 81% of total PVC production capacity (CMAI 2011b). Little information is available on PCDD/PCDF releases from this production chain other than limited data on releases from acetylene production (Lee *et al.* 2009, Jin *et al.* 2009) and in wastewater treatment sludge (USEPA 2000). More detailed descriptions of EDC, VCM and PVC production processes are given in Annex 48 and in the BAT&BEP Guidance.

### **Emission Factors**

Emission factors for production of EDC, VCM and PVC are presented in Tables II.7.7-II.7.10, according to four types of facilities – EDC/VCM/PVC facilities, EDC/VCM facilities, EDC-only facilities and PVC-only facilities. Revised or newly added emission factors are highlighted in red.

The derivation of emission factors presented in Tables II.7.7-II.7.10 is explained in Annex 48. As parties and facilities evaluate their operations they should note that any facility may have a mixture of classes of operation. Generally, analytical data should be required to support a claim of class 3.

For on-site hazardous waste incinerators and boilers used to generate heat and power, relevant information should be gathered and included in Source Group 1 – Waste Incineration and Source Group 3 – Power Generation and Heating, respectively.

**Table II.7.7 PCDD/PCDF emission factors ( $EF_{Air}$ ) for source category 7c EDC/VCM/PVC Production: Releases to Air from Vent or Liquid/Vent Combustors or Thermal Oxidizers and Halogen Acid Furnaces**

7c EDC, VCM and PVC Production	EDC, EDC/VCM and EDC/VCM/PVC Vent and Liquid-Vent Combustors or Thermal Oxidizers		PVC-Only <sup>11</sup> Vent Combustors or Thermal Oxidizers		Halogen Acid Furnaces
		Flue Gas Conc.		Flue Gas Conc.	Flue Gas Conc.
Classification	$\mu\text{g TEQ/t VCM}$	$\text{ng TEQ/Nm}^3$	$\mu\text{g TEQ/t PVC}$	$\text{ng TEQ/Nm}^3$	$\text{ng TEQ/Nm}^3$
1. Low-end technologies	5	5	1	1	0.5
2. Mid-range technologies	0.5	0.5	0.1	0.1	0.06
3. High-end technologies	0.05	0.1	0.02	0.02	0.02

**Table II.7.8 PCDD/PCDF emission factors ( $EF_{Water}$ ) for source category 7c EDC/VCM/PVC Production: Releases to Water via Wastewater Effluent**

7c EDC, VCM, and PVC Production	EDC, EDC/VCM and EDC/VCM/PVC production from sites with oxychlorination reactors <sup>A</sup>		Suspension, Dispersion or Emulsion PVC-only	
		Concentration		Concentration
Classification	$\mu\text{g TEQ/t EDC}$	$\text{ng TEQ/L effluent}$	$\mu\text{g TEQ/t PVC}$	$\text{ng TEQ/L effluent}$
1. Low-end technologies	25	5	0.03	0.01
2. Mid-range technologies	2.5	0.5	0.003	0.001
3. High-end technologies	0.5	0.1	0.0003	0.0001

<sup>A</sup> Assumes a balanced or nearly balanced direct chlorination-oxychlorination process. Sites operating direct chlorination only are ND.

**Table II.7.9 PCDD/PCDF emission factors ( $EF_{Residue}$ ) for source category 7c EDC/VCM/PVC Production: Releases to Residues**

7c EDC, VCM and PVC Production	EDC, EDC/VCM, and EDC/VCM/PVC Facilities $\mu\text{g TEQ/t EDC}$ from sites with oxychlorination reactors <sup>A</sup>		PVC-only $\mu\text{g TEQ/t PVC}$
	Waste Water Treatment Solids	Spent Catalyst	Waste Water Treatment Solids

<sup>11</sup> As used here, the term “PVC-only” refers to facilities that polymerize VCM received from other sources.

Classification	Fixed-bed <sup>B</sup>	Fluidized-bed <sup>C</sup>	Fixed-bed <sup>B</sup>	
1. Low-end technologies	0.75	4	8	0.095
2. Mid-range technologies	0.2	2	0.85	0.06
3a. High-end technologies (if solids are incinerated)	NA			
3b. High-end technologies (if solids are not incinerated)	0.095	0.4	0.02	0.005

<sup>A</sup> Assumes a balanced or nearly balanced direct chlorination-oxychlorination process. Sites operating direct chlorination only are ND.

<sup>B</sup> Solids derived from an EDC facility utilizing a fixed-bed oxychlorination catalyst

<sup>C</sup> Solids derived from an EDC facility utilizing a fluidized-bed oxychlorination catalyst

**Table II.7.10 PCDD/PCDF emission factors (EF<sub>Product</sub>) for source category 7c EDC/VCM/PVC  
Production: Releases to Products**

7c EDC, VCM and PVC Production	µg TEQ/t EDC, VCM or PVC sold			
	EDC		VCM	PVC
Classification	Produced by oxychlorination or mixed direct chlorination and oxychlorination	Produced by Direct chlorination only		
1. Low-end technologies	2	ND	NA	ND
2. Mid-range technologies	0.2	ND	NA	ND
3. High-end technologies	0.006	ND	NA	NA

### Level of confidence

Emission factors in this source category are associated with a low level of confidence for all classes, as emission factors are based on a low data range derived from a limited geographical coverage.

## 7d Chlorinated Aromatic Chemicals

### Chlorobenzenes

Chlorobenzenes are produced commercially by reacting Cl<sub>2</sub> with liquid benzene in the presence of a catalyst such as ferric chloride (FeCl<sub>3</sub>). The predominant products of this reaction are chlorobenzene, HCl, 1,2-dichlorobenzene (o-dichlorobenzene) (CAS 95-50-1) and 1,4-dichlorobenzene (p-dichlorobenzene) (CAS 106-46-7). As this direct chlorination process is continued, 1,2,4-trichlorobenzene (CAS 120-82-1), other tri-, tetra-, and pentachlorobenzenes, and, finally, hexachlorobenzene are formed. Total global production of chlorobenzenes in 2003 is estimated at 640,000 tons (China Chemical Reporter 2004).

For 1,4-dichlorobenzene, the largest use may be in the production of poly(p-phenylene) sulfide, a thermoplastic polymer in wide use because of its resistance to chemical and thermal attack. It is also used as an insecticide to control moths, moulds, mildew, and as a disinfectant and odor control agent in waste containers and restrooms (Rossberg *et al.* 2006).

### Emission Factors

A default emission factor is shown in Table II.7.11 for 1,4-Dichlorobenzene, and further details on its derivation are presented in Annex 48.

**Table II.7.11 PCDD/PCDF emission factors for source category 7d Chlorobenzene Production**

7d	Chlorobenzene Production	Emission Factors ( $\mu\text{g TEQ/t product}$ )				
		Air	Water	Land	Product	Residue
1	1,4-Dichlorobenzene (1,4-DCB, <i>p</i> -dichlorobenzene or <i>p</i> -DCB)	ND	ND	NA	39	ND

### Level of confidence

The emission factor is associated with a medium level of confidence, as it is based on a low data range; it is not based on expert judgment, but derived from a limited geographical coverage.

### Polychlorinated Biphenyls (PCBs)

The total global production of PCBs is estimated at 1.3 to 2 million tons (Breivik *et al.* 2002, Fiedler 2001). PCBs have been used for a wide range of closed applications (transformers, capacitors) and open applications (sealants, caulking, carbonless paper, plasticizers in paints and cements, casting agents, flame retardant in fabric and heat stabilizing additives for PVC electrical insulation, adhesives, railway sleepers) (Erickson and Kaley 2011). Although PCB production ceased in the 1980s, much PCB-containing equipment remains in use, materials containing PCBs are being used, and PCB wastes are still awaiting disposal.

PCDD/PCDF in commercial PCBs consist mainly of PCDF in the  $\mu\text{g/kg}$  to  $\text{mg/kg}$  range, along with low PCDD concentrations (Takasuga *et al.* 2005, Huang *et al.* 2011, Johnson *et al.* 2008, Wakimoto *et al.* 1988). The global production of 1.3 to 2 million tons PCBs contained approximately 10,400 to 16,000 kg WHO-TEQ mainly from dioxin-like PCBs (Weber *et al.* 2008). PCDD/PCDF concentrations in used PCBs are largely unknown. Limited data are available on PCDF levels in used PCBs, indicating that, for transformers, the levels might be similar as those found in used PCBs (Huang *et al.* 2011, Masuda *et al.* 1986). As shown in Table II.10.1, the dioxin-like TEQ contribution from PCDF in technical PCBs is normally below 10%. When commercial PCBs are subjected to elevated temperatures, PCDD/PCDF concentrations increase as documented for heat exchange fluids in the Yusho incident, where PCDF TEQ levels had considerably increased, reaching similar TEQ levels as for dl-PCB (Masuda *et al.* 1986). PCDF formation by thermal treatment of PCB can result in a TEQ increase of the PCB mixture of up to 50 fold (Weber 2007). Sites where PCBs are used or PCB-containing equipment is stored, dismantled or disposed of can generate local contamination and potential hotspots (see Source Group 10).

The first step in estimating the stock and releases of PCDD/PCDF associated with the use and storage of PCB-containing equipment is to compile a national inventory of the equipment and possibly other PCB legacies. Based on the PCB inventory, total TEQ in this stock can be calculated according to Table II.10.2. The inventory data can be used in combination with PCB leakage rates to estimate the quantity of PCDD/PCDF and dioxin-like PCBs released annually from the inventoried PCB equipment. The PCB leakage rates depend on a number of factors including the age of the equipment, conditions of exploitation and storage, climatic conditions etc. The precise impact of most of these factors is not well studied. For a preliminary assessment of PCB releases into the environment, emission factors given in the EMEP/EEA Atmospheric Emission Inventory Guidebook (2009) can be used (Table II.10.1).



Local circumstances will determine whether the leaked PCBs and PCDD/PCDF are released to air, water or land or sent to disposal.

### **Pentachlorophenol (PCP) and Sodium Pentachlorophenolate (PCP-Na)**

PCP or “penta” (CAS 87-86-5) and PCP-Na (CAS 131-52-2) are used as pesticides and as preservatives for *e.g.* wood (indoor and outdoor), leather, textiles (including cotton or wool) and for killing snails in areas where schistosomiasis is epidemic (Zheng *et al.* 2008, 2011). PCP is also used to produce PCP-Na and pentachlorophenol laurate (PCPL), which is used on textiles and other fabrics (van der Zande 2010).

While there are no recent data on global production, PCP production is estimated at 7,257 tons/year in the U.S. (van der Zande 2010). In 2010, Mexico produced approximately 7,000 tons/year, approximately 80% of which were exported (B. Cardenas, personal communication, 26 November 2012). In China, PCP production was of 10,000 tons/year in 1997 (Ge *et al.* 2007). PCP is produced by several methods, including the following:

1. Reaction of Cl<sub>2</sub> with liquid phenol, chlorophenol or a polychlorophenol at 30-40°C to produce 2,4,6-trichlorophenol, which is then converted to PCP by further chlorination at progressively higher temperatures in the presence of catalysts (aluminum, antimony, their chlorides, and others) (Borysiewicz 2008);
2. Alkaline hydrolysis of hexachlorobenzene (HCB) in methanol and dihydric alcohols, in water and mixtures of different solvents in an autoclave at 130 - 170°C (Borysiewicz 2008); and
3. Thermolysis of hexachlorocyclohexane (HCH), including a chlorination step and hydrolysis (Wu 1999).

PCP-Na was produced until 1984 using the alkaline hydrolysis of hexachlorobenzene. Now, however, it is produced by dissolving PCP flakes in sodium hydroxide solution (Borysiewicz 2008). It has been suggested that post-production processing of PCP flakes from the latter process accounted for more extensive exposure to PCP and its contaminants than did production (Ruder 2011).

PCDD/PCDF are by-products in all of these manufacturing methods (Borysiewicz 2008). In addition, the method based on alkaline hydrolysis of HCB can result in the presence of HCB in the resulting PCP. Commercial PCP may contain up to 0.1% of PCDD/PCDF, which are released to the air from PCP-treated products, released to water when PCP-treated textiles and other products are washed, and concentrated in the sludge of wastewater facilities that treat the washwater. PCP-derived PCDD/PCDF are released to air and land from in-service wood products, such as utility poles and railroad ties (Borysiewicz 2008), when sewage sludge is land applied, and when PCP-treated products are burned.

PCDD/PCDF may also be brought into a country through the import of PCP as well as PCP-treated products such as wood and wood products, furniture, textiles, and leather. Tracing these flows can be very difficult. The impact on emission factors of burning PCP-contaminated wood can be seen in source category 3d - Household Heating and Cooking with Biomass. PCP-treated materials also contribute to higher releases from open burning processes as can be seen in source category 6b - Waste Burning and Accidental Fires.



### Emission Factors

Emission factors for PCP and PCP-Na are presented in Table II.7.14. Revised or newly added emission factors are highlighted in red. For the use of PCP for agricultural or related purposes, releases to land of PCDD/PCDF can be estimated by using the  $EF_{\text{Product}}$  as  $EF_{\text{Land}}$ .

**Table II.7.14 PCDD/PCDF Emission Factors for source category 7d PCP and PCP-Na Production**

7d	PCP and PCP-Na Production	Emission Factors ( $\mu\text{g TEQ/t product}$ )				
		Air	Water	Land	Product	Residue
1	Pentachlorophenol (PCP)	ND	ND	ND	634,000	ND
2	Pentachlorophenol, sodium salt (PCP-Na)	ND	ND	ND	12,500	ND

### Level of Confidence

Emission factors in this source category are associated with a medium level of confidence, as they are based on a low data range and are derived from a limited geographical coverage.

### 2,4,5-Trichlorophenoxyacetic Acid (2,4,5-T) and 2,4,6-Trichlorophenol

2,4,5-T (CAS 93-76-5), an herbicide used primarily as a defoliant, is the most important derivative of 2,4,5-trichlorophenol (CAS 95-95-4). Today, there are only a few production sites of trichlorophenol. While 2,4,5-T is widely perceived as being contaminated with only 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), substantial concentrations of other PCDD/PCDF congeners have been identified (Pignatello and Huang 1993).

Hotspots in soil that may exist at former 2,4,5-T production, storage and handling sites should be addressed in Source Group 10 – Contaminated Sites and Hotspots.

### Emission Factors

Due to lack of data, emission factors have been derived only for releases in products, as shown in Table II.7.15. For the use of 2,4,5-T for agricultural or related purposes, releases to land of PCDD/PCDF can be estimated by using the  $EF_{\text{Product}}$  as  $EF_{\text{Land}}$ .

**Table II.7.15 PCDD/PCDF Emission Factors for source category 7d 2,4,5-T and 2,4,6-Trichlorophenol Production**

7d	2,4,5-T and 2,4,6-Trichlorophenol Production	Emission Factors ( $\mu\text{g TEQ/t product}$ )				
		Air	Water	Land	Product	Residue
1	2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	ND	ND	ND	7,000	ND
2	2,4,6-Trichlorophenol	ND	ND	ND	700	ND

### Level of confidence

Emission factors are associated with a medium level of confidence, as they are based on a low data range; they are not based on expert judgment, but are derived from a limited geographical coverage.

### Chloronitrofen, Chlornitrofen, or 2,4,6-Trichlorophenyl-4-nitrophenylether (CNP)

CNP (CAS 1836-77-7) has been used as an alternative for pentachlorophenol and applied extensively in rice paddies in Japan. Production of CNP begins with the production of 2,4,6-trichlorophenol (CAS 88-06-2). 2,4,6-trichlorophenol is reacted with potassium hydroxide to form

potassium 2,4,6-trichlorophenolate. The latter chemical is reacted with 4-fluoronitrobenzene in the presence of a copper catalyst to form 2,4,6-trichlorophenyl *p*-nitrophenyl ether (Suzuki and Nagao 2005).

### Emission Factors

Due to insufficient information, only emission factors for releases in product were derived, as shown in Table II.7.16. Revised or newly added emission factors are highlighted in red. For the use of CNP for agricultural or related purposes, releases to land of PCDD/PCDF can be estimated by using the  $EF_{\text{Product}}$  as  $EF_{\text{Land}}$ .

**Table II.7.16 PCDD/PCDF Emission Factors for source category 7d CNP Production**

7d	CNP Production Classification	Emission Factors (µg TEQ/t product)				
		Air	Water	Land	Product	Residue
1	Low-end technologies	ND	ND	ND	9,200,000	ND
2	Mid-range technologies	ND	ND	ND	4,500	ND

### Level of confidence

Emission factors are associated with a medium level of confidence, as they are based on a low data range; they are not based on expert judgment, but are derived from a limited geographical coverage.

### Pentachloronitrobenzene (PCNB) (Quintozene)

PCNB (CAS 82-68-8), also known by other names including quintozene and terrachlor, is a broad-spectrum, contact fungicide used on a wide range of crops, such as turf, peanuts, cole crops (e.g., cabbage), rice, potatoes and cotton. It is used to treat both soil and seeds as well as for foliar application. However, due in part to PCDD/PCDF contamination, PCNB has been banned for a variety of uses in several countries, including the U.S., Canada, Japan and Germany.

PCNB is produced by the reaction in chlorosulfuric acid of nitrobenzene and Cl<sub>2</sub> with iodine as a catalyst. PCNB can also be produced by the nitration of pentachlorobenzene.

High concentrations of PCDD/PCDF have been detected in studies conducted in Australia (Holt *et al.* 2010), China (Huang *et al.* 2012), and Japan (MAFF 2002). The latter two studies also found high concentrations of dioxin-like PCBs. In addition, a study of PCNB exposure to sunlight found that PCDD/PCDF TEQ increased by more than 800% (Holt *et al.* 2011).

### Emission Factors

For the production of PCNB, PCDD/PCDF emission factors are shown in Table II.7.17 and PCB emission factors are shown in Annex 48. Revised or newly added emission factors are highlighted in red.

For the use of PCNB is for agricultural or related purposes, release to land of both PCDD/PCDF and PCBs can be estimated by using the  $EF_{\text{Product}}$  as  $EF_{\text{Land}}$ . Similarly, for aquacultural or related purposes, release to water can be estimated by using the  $EF_{\text{Product}}$  as  $EF_{\text{Water}}$ .

**Table II.7.17 PCDD/PCDF Emission Factors for source category 7d Pentachloronitrobenzene Production**

7d	Pentachloronitrobenzene Production Classification	Emission Factors (µg TEQ/t product)				
		Air	Water	Land	Product	Residue

1	Low-end production technologies	ND	ND	ND	5,600	ND
2	Mid-range production technologies	ND	ND	ND	2,600	ND
3	High-end production technologies	ND	ND	ND	260	ND

### Level of confidence

Emission factors in this section are associated with a medium level of confidence, as emission factors are based on a moderate data range with a broad geographical distribution.

### 2,4-Dichlorophenoxyacetic Acid (2,4-D) and Derivatives

2,4-Dichlorophenoxyacetic acid (2,4-D, CAS 94-75-7) and its derivatives are systemic herbicides used to control broadleaf weeds. 2,4-D is one of the world's most widely used pesticides (Industry Task Force 2012).

2,4-D is commonly prepared by the condensation of 2,4-dichlorophenol with monochloroacetic acid in a strongly alkaline medium at moderate temperatures. It is also produced by the chlorination of phenoxyacetic acid, but this method leads to a product with a high content of 2,4-dichlorophenol and other impurities. Higher reaction temperatures and alkaline conditions during the manufacture of 2,4-D increase the formation of PCDD/F. The alkali metal salts of 2,4-D are produced by the reaction of 2,4-D with the appropriate metal base. Amine salts are obtained by reacting amine and 2,4-D in a compatible solvent. Esters are formed by acid-catalysed esterification with azeotropic distillation of water or by direct synthesis in which the appropriate ester of monochloroacetic acid is reacted with dichlorophenol to form the 2,4-D ester (IPCS 1989). The following include some of the more commonly used derivatives of 2,4-D: 2,4-D sodium salt (CAS 2702-72-9); 2,4-D diethyl amine (CAS 2008-39-1); 2,4-D dimethylamine salt (CAS 2008-39-1); 2,4-D isopropyl ester (CAS 94-11-1); 2,4-D triisopropyl acid; 2,4-D butoxyethyl ester (CAS 1929-73-3); 2,4-D isooctyl ester (CAS 25168-26-7); and 2,4-D ethylhexyl ester (CAS 1928-43-4). 2,4-D was first marketed in 1944. Off-patent for many years, 2,4-D and its derivatives are manufactured by many different companies around the world.

### Emission Factors

For the production of 2,4-D and its derivatives, PCDD/PCDF emission factors are presented in Table II.7.18. Revised or newly added emission factors are highlighted in red.

For uses of 2,4-D and its derivatives for agricultural or related purposes, release to land can be estimated by using the  $EF_{\text{Product}}$  as  $EF_{\text{Land}}$ . Similarly, for aquacultural uses, release to water can be estimated by using the  $EF_{\text{Product}}$  as  $EF_{\text{Water}}$ .

**Table II.7.18 PCDD/PCDF Emission Factors for source category 7d 2,4-D and Derivatives**

7d	2,4-D and Derivatives	Emission Factors ( $\mu\text{g TEQ/t product}$ )				
		Air	Water	Land	Product	Residue
1	Low-end production technologies	ND	ND	ND	5,688	ND
2	Mid-range production technologies	ND	ND	ND	170	ND
3	High-end production technologies	ND	ND	ND	0.1	ND

### Level of confidence

Emission factors in this section are associated with a medium level of confidence, as emission factors are based on a moderate data range with a broad geographical distribution.

More detailed information on PCDD/PCDF contamination of other organochlorine pesticides can be found in Annex 2.

### Chlorinated Paraffins (CPs)

CPs are straight-chain hydrocarbons that have been chlorinated. Chlorinated paraffins are classified according to their carbon-chain length and percentage of chlorination, with carbon-chain lengths generally ranging from C<sub>10</sub> to C<sub>30</sub> and chlorination from approximately 35% to greater than 70% by weight. Around 40 CAS numbers have been used to describe the whole chlorinated paraffin family, *e.g.*, CPs of unspecified length are CAS 63449-39-8.

CPs are made by reacting Cl<sub>2</sub> with paraffin fractions obtained from petroleum distillation. The three most common commercial feedstocks used are short-chain (C<sub>10-13</sub>), medium-chain (C<sub>14-17</sub>) and long-chain (C<sub>18-30</sub>) paraffins. Global production of CPs is estimated at 1 million tons/yr, some 70% of which is produced in China (Takasuga *et al.* 2012). The largest use of CPs is in industrial cutting fluids, particularly in the manufacture of automobiles and automobile parts. In addition, they are used in commercial paints, adhesives, sealant and caulks as well as plasticizers in PVC and flame retardants in other plastics and rubber. Relatively high concentrations of PCDD/PCDF, total PCBs and HCB have been reported in samples of technical long-chain CPs (Takasuga *et al.* 2012).

### Emission Factors

For the production of CPs, PCDD/PCDF emission factors are shown in Table II.7.19. Revised or newly added emission factors are highlighted in red. Emission factors for other unintentional POPs releases are presented in Annex 48.

**Table II.7.19 PCDD/PCDF Emission Factors for source category 7d Chlorinated Paraffins Production**

7d	Chlorinated Paraffins Production	Emission Factors (µg TEQ/t product)				
		Air	Water	Land	Product	Residue
	<b>Classification</b>					
1	Low-end production technologies	ND	ND	ND	ND	ND
2	Mid-range production technologies	ND	ND	ND	500	ND
3	High-end production technologies	ND	ND	ND	140	ND

### Level of confidence

Emission factors in this section are associated with a low level of confidence, as emission factors are based on a small data range with a limited geographical distribution.

### *p*-Chloranil (2,3,5,6-tetrachloro-2,5-cyclohexadiene-1,2-dione)

*p*-Chloranil (CAS 118-75-2) is used as an intermediate in the production of medicines, pesticides, and dioxazine dyes. It is also used as a fungicide and for seed treatment, although such uses are prohibited in some countries. In China, about 2,000 tons of chloranil are produced and used as a fungicide, as an intermediate in the synthesis of medicines and pesticides, and as an oxidizing agent used in organic synthesis, particularly for dye intermediates (Liu *et al.* 2012). Two methods for producing *p*-chloranil are as follows:

1. The process of direct chlorination of phenol using Cl<sub>2</sub>, which produces both *o*- and *p*-chloranil was developed and used in Germany until 1990. This may still be used by producers in other countries.

2. The more widely used process begins with the conversion of phenol to hydroquinone, followed by the reaction of hydroquinone with Cl<sub>2</sub> or hydrogen peroxide and hydrochloric acid to form *p*-chloranil.

PCDD/PCDF contamination in chloranil is transferred to dyestuffs, pigments, inks, etc. and other products made from chloranil (see chloranil-derived pigments and dyes below). PCDD/PCDF in chloranil-derived materials are further transferred into the production processes of textiles, polymers/plastics, and packaging materials (paper, tin cans, etc.) and released in process outputs (see, for example, Source Category 7g – Textile Production). When textiles, clothing and other consumer goods treated with chloranil-based pigments and dyes are washed, some portion of the PCDD/PCDF is carried into domestic and municipal wastewater, where it contributes to PCDD/PCDF in wastewater treatment effluents and sludge. When the consumer goods are discarded or recycled, the PCDD/PCDF that originated during chloranil production adds to PCDD/PCDF contamination in disposal and recycling processes. In paper recycling and textile production and dyeing, PCDD/PCDF will be released into water and/or concentrated in the residue (sludge).

### Emission Factors

Due to lack of data, emission factors for *p*-chloranil are derived only for releases to product. Revised or newly added emission factors are highlighted in red.

**Table II.7.20 PCDD/PCDF Emission Factors for source category 7d *p*-Chloranil Production**

7d	<i>p</i> -Chloranil Production	Emission Factors (µg TEQ/t product)				
		Air	Water	Land	Product	Residue
1	Direct chlorination of phenol	ND	ND	ND	400,000	ND
2	Chlorination of hydroquinone with minimal purification	ND	ND	ND	<b>1,500,000</b>	ND
3	Chlorination of hydroquinone with moderate purification	ND	ND	ND	<b>26,000</b>	ND
4	Chlorination of hydroquinone with advanced purification	ND	ND	ND	<b>150</b>	ND

### Level of confidence

Emission factors are associated with a medium level of confidence, as they are based on a low data range; they are not based on expert judgment, but are derived from a limited geographical coverage.

### Phthalocyanine dyes and pigments

Phthalocyanine dyes and pigments had a global production rate of about 420,000 tons in 2011 (Linak *et al.* 2011, The Freedonia Group 2009). They are prepared by variations of the following methods:

- Reaction of phthalonitrile with metal or metal salts;
- Reaction of phthalic anhydride, phthalic acid or phthalimide, tetrachlorophthalic anhydride with *e.g.* specific organics, urea, metal salt and catalyst;
- Reaction of metal-free phthalocyanine or replaceable metal phthalocyanine with another metal.

Copper phthalocyanine, a blue pigment, is generally produced using the second method. The phthalic anhydride/imide, a metal salt, urea and a catalyst are heated at 170-200°C for about four hours in a solvent such as trichlorobenzene, nitrobenzene or chloronaphthalene. The blue of copper phthalocyanine is shifted towards green by replacing hydrogen atoms on the aromatic rings with chlorine (*e.g.* pigment green 7) or chlorine and bromine (*e.g.* pigment green 36). This is accomplished through direct chlorination of copper phthalocyanine by passing Cl<sub>2</sub> into an AlCl<sub>3</sub>/NaCl mixture at 180-200°C (Jain 2011). PCDD/PCDF have been detected in samples of copper phthalocyanine and phthalocyanine green (Ni *et al.* 2005), as well as nickel phthalocyanine (Hutzinger and Fiedler 1991).

### Emission Factors

Due to lack of data, PCDD/PCDF emission factors for phthalocyanine-derived dyes and pigments are presented only for releases in products. Revised or newly added emission factors are highlighted in red. Emission factors for other unintentional POPs are included in Annex 48.

**Table II.7.21 PCDD/PCDF Emission Factors for source category 7d Phthalocyanine Dyes and Pigments Production**

7d	Phthalocyanine Dyes and Pigments Production	Emission Factors (µg TEQ/t product)				
		Air	Water	Land	Product	Residue
	<b>Classification</b>					
1	Phthalocyanine copper (CAS 147-14-8)	ND	ND	ND	70	ND
2	Phthalocyanine green (CAS 1328-45-6)	ND	ND	ND	1,400	ND

### Tetrachlorophthalic acid (TCPA) and related pigments

TCPA is the primary feedstock for the production of a range of pigments. While no PCDD/PCDF data are available for TCPA, unintentional HCB concentrations as high as 3,000,000 µg/kg have been detected (Government of Japan 2006, 2007). Additional information on HCB concentrations in TCPA and corresponding emission factors are included in Annex 48.

### Dioxazine dyes and pigments

Dioxazine dyes and pigments are produced through the reaction of *p*-chloranil with aromatic amines in the presence of a base. Tests on some of these dyes and pigments in the early 1990s showed PCDD/PCDF concentrations in the range 1 to 60 µg TEQ/kg, attributed to the use of PCDD/PCDF-contaminated *p*-chloranil produced by the chlorination of phenol (US EPA 2006a, Krizanec and Le Marechal 2006). Subsequently, an alternate process was developed for producing chloranil with lower PCDD/PCDF content through the reaction of hydroquinone with HCl. Dioxazine pigments and dyes made using the more contaminated chloranil are listed in Table II.7.22, along with their PCDD/PCDF content. Revised or newly added emission factors are highlighted in red.

**Table II.7.22 PCDD/PCDF Emission Factors for source category 7d Dioxazine-Based Pigments Production**

7d	Dioxazine-Based Pigments Production	Emission Factors (µg TEQ/t product)				
		Air	Water	Land	Product	Residue
	<b>Classification</b>					
1	Blue 106 (CAS 6527-70-4)	ND	ND	ND	35,000	ND
2	Blue 108 (CAS 1324-58-9)	ND	ND	ND	100	ND
3	Violet 23 (Carbazole violet) (CAS 6358-30-1)	ND	ND	ND	12,000	ND

### Level of confidence

Emission factors are associated with a medium level of confidence, as they are based on a low data range; they are not based on expert judgment, but are derived from a limited geographical coverage.

### Triclosan [5-chloro-2-(2,4-dichlorophenoxy)phenol]

Triclosan (CAS 3380-34-5), a chlorophenoxy derivative, is produced by the reaction of 2,4,4'-trichloro-2'-methoxydiphenyl ether with aluminum chloride in benzene. Triclosan is used globally as an antibacterial and antifungal agent in consumer products, including soaps, deodorants, toothpastes, shaving creams, mouth washes, and cleaning supplies. It is also infused in an increasing number of consumer products, such as kitchen utensils, toys, bedding, socks, and trash bags.

### Emission Factors

Emission factors are derived for three classes of production of triclosan. Revised or newly added emission factors are highlighted in red.

**Table II.7.23 PCDD/PCDF Emission Factors for source category 7d Triclosan Production**

7d	Triclosan Production	Emission Factors ( $\mu\text{g TEQ/t product}$ )				
		Air	Water	Land	Product	Residue
1	Low-end technologies	ND	ND	ND	1,700	82,000
2	Mid-range technologies	ND	ND	ND	60	ND
3	High-end technologies	ND	ND	ND	3	ND

### Level of confidence

Emission factors are associated with a medium level of confidence, as they are based on a low data range; they are not based on expert judgment, but are derived from a limited geographical coverage.

## 7e Other Chlorinated and Non-Chlorinated Chemicals

### Titanium Tetrachloride ( $\text{TiCl}_4$ ) and Titanium Dioxide ( $\text{TiO}_2$ )

$\text{TiO}_2$  (CAS 13463-67-7) is the world's most widely used white pigment, with global production estimated to be 5 million tons in 2007 (USGS 2008). About 50% of  $\text{TiO}_2$  is used in paints, varnishes and lacquer; 25% in paper and paperboard; and 20% in plastics (USEPA 2001).

$\text{TiO}_2$  is produced from  $\text{TiO}_2$ -rich ores, such as rutile or ilmenite, by either of two processes:

- The sulfate process entails digesting ilmenite ore or  $\text{TiO}_2$ -rich slag with sulfuric acid to produce a cake, which is purified and calcined to produce  $\text{TiO}_2$  pigment. This process is less commonly used because it generates sulfuric acid wastes in as much as two times the product weight, resulting in the need for expensive treatment by neutralization before disposal of the wastes (UNEP 2007, USEPA 1995).
- The chloride process entails reacting elemental chlorine with rutile or high-grade ilmenite at 850°C to 950°C, using petroleum coke as a reductant. This produces  $\text{TiCl}_4$  (CAS 7550-45-0) gas, which is then oxidized to form purified  $\text{TiO}_2$ . The chloride process is most commonly used due to its relative compactness, recycling of process materials, better product properties, and considerably lower generation of waste (UNEP 2007, USEPA 1995).



PCDD/PCDF formation is known to occur in the chloride process (Lakshmanan *et al.* 2004), and PCDD/PCDF have been detected in treated wastewater, wastewater treatment sludge, and filter press solids (USEPA 2001).

### Emission Factors

Emission factors are derived for TiO<sub>2</sub> production via the chloride process and presented in Table II.7.24. Revised or newly added emission factors are highlighted in red.

**Table II.7.24 PCDD/PCDF Emission Factors for source category 7e TiCl<sub>4</sub> and TiO<sub>2</sub> Production via the Chloride Process**

7e	TiCl <sub>4</sub> and TiO <sub>2</sub> Production	Emission Factors (µg TEQ/t product)				
		Air	Water	Land	Product	Residue
	Classification					
1	Low-end technology	ND	0.2	ND	0.0	42
2	High-end technology	ND	0.001	ND	0.0	8

### Level of confidence

Emission factors are associated with a medium level of confidence, as they are based on a low data range; they are not based on expert judgment, but are derived from a limited geographical coverage.

### Caprolactam (2-Azacycloheptanone)

Caprolactam (CAS 105-60-2) is produced commercially by two methods. Only one entails the use of chlorine in some form: the reaction of HCl with nitrosylsulfuric acid to produce nitrosyl chloride which is then reacted with cyclohexane and HCl to produce cyclohexanone which undergoes further reactions to produce caprolactam. In 2010, global production of caprolactam was 3.8 million metric tons (SRI Consulting 2011). Virtually all caprolactam is used to produce Nylon 6. PCDD/PCDF have been detected in air emissions, process wastewater and in treated wastewater from caprolactam production facilities in two countries (Lee *et al.* 2009, Kawamoto 2002, Hong and Xu 2012). These findings suggest that PCDD/PCDF are likely also to occur in residues, including those from wastewater treatment.

### Emission Factors

**Table II.7.25 PCDD/PCDF Emission Factors for source category 7e Caprolactam Production**

7e	Caprolactam Production	Emission Factors (µg TEQ/t product)				
		Air	Water	Land	Product	Residue
1	Caprolactam	0.00035	0.50 µg TEQ/L	ND	ND	ND

### Level of confidence

Emission factors are associated with a medium level of confidence, as they are based on a low data range; they are not based on expert judgment, but are derived from a limited geographical coverage.

## 7f Petroleum Refining

The petroleum refining industry converts crude oil into refined products, including liquefied petroleum gas, gasoline, kerosene, aviation fuel, diesel fuel, fuel oils, lubricating oils, bitumen and feedstock for the petrochemical industry. The composition of petroleum (crude oil) can vary significantly depending on its source.



Petroleum refining processes that have been identified as PCDD/PCDF sources include the following (RTI International 2011, Jacobs Consultancy 2002):

- Stationary combustion sources, such as boilers and process heaters, generate heat and power by burning fuels derived from refinery processes; these sources are addressed in Source Group 3 Power Generation and Heating. Particular attention is needed in the development of the PCDD/PCDF inventory for this source category to avoid double counting of releases from power boilers.
- Coking units use heat to thermally crack heavy hydrocarbon streams to form lighter, more useful distillates such as heating oils or gasoline. Traditional fluid coking units are one of the largest vent emissions sources at a refinery, being comparable to emissions from the CCU regenerator.
- Catalytic reforming units are a series of catalytic reactors that turn naphtha into high-octane gasoline. The catalyst accumulates carbon (coke) so that it must be regenerated. In the continuous process, aged catalyst is continuously moved from the reactor to the regenerator where the carbon is burned from the catalyst with hot air/steam. Chlorine or organochlorines, such as tri- or perchloroethylene, are added to retain catalytic activity. While the catalytic reactors have no direct process vents, the catalyst regenerators do have such vents.
- Flares are compulsory safety equipment used both for safety reasons during upsets, start-up, shut down, and system blow-down and for managing the disposal of waste gases from routine operations.

PCDD/PCDF may be released to air from vent stacks and flares, captured in scrubbing systems and released to water in treated effluents, and released in residues such as exhausted catalysts and wastewater treatment sludge.

### Emission Factors

Emission factors for calculating releases of PCDD and PCDF from petroleum refineries are presented below for the following processes:

- Flaring of gases released from the petroleum industry
- Catalytic reforming unit (including catalyst regenerator)
- Coking unit
- Refinery-wide wastewater treatment

PCDD/PCDF emission factors are listed in Tables II.7.26 and II.7.27. Revised or newly added emission factors are highlighted in red. Detailed information on the derivation of these emission factors can be found in Annex 49.

**Table II.7.26 PCDD/PCDF emission factors for source category 7f Petroleum Refining (flaring of gases)**

7f	Petroleum Refining (flares)	EF <sub>Air</sub> µg TEQ/TJ fuel burned
<b>Classification</b>		
1	Flares	<b>0.25</b>

**Table II.7.27 PCDD/PCDF emission factors for source category 7f Petroleum Refining (production processes)**

7f	Petroleum Refining (production processes)	Emission Factors				
Classification		Air µg TEQ/t oil <sup>A</sup>	Water pg TEQ/L	Land	Product	Residue µg TEQ/t residue
1	Catalytic reforming unit (including catalyst regenerator)	0.017	NA	NA	NA	14
2	Coking unit	0.41	NA	NA	NA	ND
3	Refinery-wide wastewater treatment	ND	5	ND	ND	ND

<sup>A</sup> Mass of oil specific to each processing unit

### Level of confidence

Emission factors for this source category are associated with a medium level of confidence for all classes, as they are based on a low data range, but not based on expert judgment, and are derived based on a limited geographical coverage.

## 7g Textile Production

The textile industry is one of the longest and most complicated industrial chains in the manufacturing sector. It is a diverse, fragmented group of establishments that produce and/or process textile-related products, such as fiber, yarn, and fabric, for further processing into finished goods. These establishments range from small “back street” operations with few controls to large-scale highly sophisticated industrial operations with comprehensive pollution controls. Because the processes for converting raw fibers into finished products are complex, most textile mills specialize (USEPA 1997b).

Textile production industries are potential sources of PCDD/PCDF due to a number of factors:

- Raw materials may be contaminated with PCDD/PCDF due to treatment with PCDD/PCDF-contaminated pesticides, such as pentachlorophenol;
- Dyes and pigments used on fibers and textiles may be contaminated with PCDD/PCDF, for example, dioxazine dyes produced from chloranil and phthalocyanine-based pigments;
- Finishing processes may include the use of PCDD/PCDF-contaminated chemicals, such as Triclosan, an antimicrobial agent;
- Boilers and heaters may be used for power and heat generation (see Source Group 3);
- Incinerators may be used for disposal of process residues;
- Large volumes of effluent water are released into the environment.
- Formation of PCDD/PCDF during finishing (Križanec *et al.* 2005).

Details on textile production processes are presented in the BAT&BEP Guidance.

### Emission Factors

PCDD/PCDF have been detected in air emissions, wastewater and wastewater treatment sludge from textile mills. However, currently available data are not sufficient to support the derivation of emission factors for these vectors. PCDD/PCDF emission factors for two source classes of products are listed in Table II.7.28. The derivation of these emission factors as well as discussion of existing information on releases to air, water and wastewater treatment sludge are addressed in Annex 50.

**Table II.7.28 PCDD/PCDF emission factors for source category 7g Textile Production**

7g	Textile Production	Emission Factors (µg TEQ/t textile)				
		Air	Water	Land	Product	Residue
	<b>Classification</b>					
1	Low-end technology	ND	ND	ND	100	ND
2	Mid-range, non-BAT technology <sup>A</sup>	ND	ND	ND	0.1	ND
3	High-end, BAT technology	NA	NA	NA	NA	NA

<sup>A</sup>Textile technology that does not involve either formation of PCDD/PCDF or transfer from another vector.

### Level of confidence

Emission factors for this source category are associated with a low level of confidence for all classes, due to scarcity and lack of representativeness of data.

## 7h Leather refining

The tannery operation consists of converting the raw skin or hide of an animal into leather for use in the manufacture of a wide range of products. This involves a sequence of complex chemical reactions and mechanical processes. Amongst these, tanning is the fundamental stage, which gives leather its stability and essential character. The tanning industry is a potentially pollution-intensive industry with environmental concerns that include air emissions, wastewater, and solid waste.

PCDD/PCDF have been detected in finished leather goods. Evidence suggests that the sources of PCDD/PCDF are contaminated dyes, such as those derived from chloranil, and contaminated biocides, such as PCP. While leather production processes have not been evaluated for PCDD/PCDF formation or occurrence, the use of PCDD/PCDF-contaminated dyes and biocides chemicals can be expected to result in the occurrence of PCDD/PCDF in process wastewater and sludges from wastewater treatment. Also, new formation of PCDD/PCDF may occur in the leather production chain where process wastewater is treated and where wastewater treatment sludge and other process wastes are incinerated.

Leather production processes are described in greater detail in Annex 51 and in the BAT&BEP Guidelines.

### Emission Factors

Emission factors for PCDD/PCDF releases to air, water, land, and residues could not be derived due to lack of information. However, the quantities, methods of treatment, and fate of wastewater, treated wastewater effluents, wastewater treatment sludge, and other solid wastes should be noted to the extent possible since releases to water and residues could be high. If wastewater treatment sludge and/or other wastes are incinerated or otherwise combusted, this should also be noted since release to air and in residues could be high.

Emission factors for release to products are given in Table II.7.29. The derivation of these emission factors is addressed in Annex 51.

**Table II.7.29 PCDD/PCDF emission factors for source category 7h Leather Refining**

7h	Leather Refining	Emission Factors ( $\mu\text{g TEQ/t leather}$ )				
		Air	Water	Land	Product	Residue
1	Low-end technology	ND	ND	ND	1,000	ND
2	Mid-range technology	ND	ND	ND	10	ND

#### **Level of confidence**

Emission factors for this source category are associated with a low level of confidence for all classes, due to scarcity and lack of representativeness of data.

## 8 – Miscellaneous

This category comprises five processes, shown in Table II.8.1, that were not placed in other source groups for various reasons. For example, two of the processes – drying of green fodder and smoke houses – are included here even though they are combustion processes that might be considered to be similar to processes addressed in source category 1f Waste wood combustion or source category 3d Household heating and cooking. These are shown in Table II.8.1.

**Table II.8.1 Overview of source categories included in group 8 – Miscellaneous**

8 – Miscellaneous		Potential release route				
		Air	Water	Land	Product	Residue
a	Drying of Biomass	x			x	x
b	Crematoria	x				x
c	Smoke houses	x			x	x
d	Dry cleaning		x		x	x
e	Tobacco smoking	x				x

With relevance to the provisions of Article 5, sources in this category can be classified as follows:

**Table II.8.2 Relevance to Article 5, Annex C of the Stockholm Convention**

No	Toolkit source category	Part II	Part III	Relevant source category in Annex C
8b	Crematoria		x	Crematoria

An example of elaborating source inventory and release estimate for this source group is included in the example inventory 9.

### 8a Drying of Biomass

Drying of woody or herbaceous biomass, *e.g.* wood chips or green fodder, occurs either with or without containment, in which the combustion gases contaminated with unintentional POPs enter in contact with the material being dried.

Other processes that use direct heating methods (*e.g.* for foodstuffs) should be addressed under source category 8c smoke houses. Processes without contact should be addressed in Source Group 3 Power Generation and Heating.

Under controlled conditions, clean fuels such as wood are used. The drying of green fodder using poor fuels, *e.g.*, treated wood, used textiles, carpets, etc., may lead to PCDD/PCDF formation and contamination of the fodder. For example, in 2005, in Germany, it was shown that the use of contaminated wood as fuel had resulted in very high concentrations of PCDD/PCDF in the fodder. When such contaminated fodder is fed to livestock, PCDD/PCDF can be transferred to the human food chain.

#### Emission Factors

PCDD/PCDF emission factors for three source classes are listed in Table II.8.3. Revised or newly added emission factors are highlighted in red. Detailed information on how these emission factors have been derived can be found in Annex 52.

### Guidance for classification of sources

**Class 1** is applied when using highly contaminated fuel (PCP- or otherwise treated material).

**Class 2** is applied when using moderately contaminated fuel.

**Class 3** is applied when using clean fuel.

**Table II.8.3 PCDD/PCDF emission factors for source category 8a Drying of Biomass**

8a	Drying of Biomass	Emission Factors (µg TEQ/t dry product)				Concentration (µg TEQ/t ash)
		Air	Water	Land	Product	Residue
1	Highly contaminated fuel (PCP- or otherwise treated material)	10	NA	ND	0.5	<b>2000</b>
2	Moderately contaminated fuel	0.1	NA	ND	0.1	<b>20</b>
3	Clean fuel	<b>0.01</b>	NA	ND	0.1*	<b>5</b>

\* For herbaceous biomass being dried, use an EF<sub>Product</sub> of 1 µg TEQ/t dry product

### Activity rates

- Agricultural institutions or feedingstuff producers;
- National statistics on energy sources;
- Surveys addressed to biomass producers.

### Level of confidence

The emission factors for this source category have been assigned a low level of confidence based on the scarcity of data and limited accessibility of activity information. Expert judgment has also been used in deriving these emission factors.

## 8b Crematoria

Cremation, reducing human bodies to ashes by burning, is a common practice in many societies. The essential components for cremation are the coffin (and the corpse), the main combustion chamber, and where applicable the afterburning chamber and air pollution control system. The cremation process is described in detail in the BAT&BEP Guidelines. The Guidelines equally provide information on PCDD/PCDF emissions from this process.

### Emission Factors

PCDD/PCDF emission factors for three source classes are listed in Table II.8.4. Detailed information on how these emission factors have been derived can be found in Annex 52.

### Guidance for classification of sources

**Class 1** includes facilities with only one burner, small combustion chamber, poor combustion conditions, e.g., temperatures below 850°C, uncontrolled combustion air flow, etc., if plastic or other decoration materials are burned together with the coffin, if the wood of the coffin has been treated with wood preservatives, or if there is no flue gas cleaning system in place.

**Class 2** includes facilities where the combustion conditions are better – temperatures securely above 850°C, controlled combustion air flow, no plastics or other problematic input materials - and some dust removal is in place. This class also includes open air cremations.

**Class 3** includes state-of-the-art facilities with sophisticated air pollution control systems.

**Table II.8.4 PCDD/PCDF emission factors for source category 8b Crematoria**

8b	Crematoria	Emission Factors ( $\mu\text{g TEQ per cremation}$ )				
		Air	Water	Land	Product	Residue
	<b>Classification</b>					
1	No control	90	NA	NA	NA	ND
2	Medium control or open air cremations	10	NA	NA	NA	2.5
3	Optimal control	0.4	NA	NA	NA	2.5

### Activity rates

- Operators of crematoria (via questionnaires) in case of few large crematoria in the country;
- National statistics on number of deceased per year and expert judgment with regards to the percentage of cremation;
- Centralized data collection on federal or provincial government level.

### Level of confidence

Class 1 emission factors are assigned a low level of confidence due to the low stability of the process, and only a limited number of measurements being available. Class 2 emission factors are assigned a medium level of confidence due to the larger range of the data. Finally, Class 3 emission factors are assigned a high level of confidence due to availability of consistent datasets from measurements with high geographical coverage.

## 8c Smoke Houses

Smoking food for preservation of meat and fish is a common practice in many countries. Smoke houses are commonly small installations that use wood as fuel and have sub-optimal combustion conditions.

### Emission Factors

PCDD/PCDF emission factors for three source classes are listed in Table II.8.5. For smoking foodstuffs in open air, use the  $EF_{\text{Air}}$  from source category 3d, class 5 (open fire three stone stoves). Detailed information on how these emission factors have been derived can be found in Annex 52.

### Guidance for classification of sources

**Class 1** should be applied if treated wood or other contaminated biomass is used as fuel.

**Class 2** should be used if clean wood or other biomass is used as fuel.

**Class 3** should be applied if clean wood or other biomass is used as fuel and there is a state-of-the-art air pollution control system in operation.

**Table II.8.5 PCDD/PCDF emission factors for source category 8c Smoke Houses**

8c	Smoke Houses	Emission Factors ( $\mu\text{g TEQ/t product}$ )				Concentration (ng TEQ/kg ash)
		Air	Water	Land	Product	Residue
	<b>Classification</b>					
1	Contaminated fuels	50	NA	NA	ND	2,000

2	Clean fuels, no afterburner	6	NA	NA	ND	20
3	Clean fuels, afterburner	0.6	NA	NA	ND	20

### Activity rates

- National statistics;
- Local producers of smoked foodstuffs;
- Surveys sent to/interviews with local producers.

### Level of confidence

The emission factors for this source category have been assigned a low level of confidence based on the scarcity of available data. Expert judgment has also been used in deriving these emission factors.

## 8d Dry Cleaning

PCDD/PCDF have been detected in the distillation residues from dry cleaning (cleaning of textiles with organic solvents, not washing with water). The PCDD/PCDF sources have been identified as the use of contaminated biocides, such as PCP, to protect textiles or raw materials – wool, cotton, etc. – and the use on textiles of PCDD/PCDF-contaminated dyes and pigments. The dry cleaning process itself does not generate PCDD/PCDF, but rather redistributes PCDD/PCDF already present in the textiles via prior contamination.

During the dry cleaning process, PCDD/PCDF are extracted from the textiles and transferred into the cleaning solvent. When the solvent is distilled for recovery and reuse, PCDD/PCDF are concentrated in distillation residues, which normally are disposed of. Detailed research has shown that PCDD/PCDF concentrations in the distillation residues do not depend on the solvent present in the dry cleaning process (Fuchs *et al.* 1990, Towara *et al.* 1992). Therefore, the influence of the solvent used is negligible; typical solvents are perchloroethylene, petrol, or fluorocarbons.

### Emission Factors

PCDD/PCDF emission factors for two source classes are listed in Table II.8.6. Detailed information on the derivation of these emission factors can be found in Annex 52.

### Guidance for classification of sources

**Class 1** includes dry cleaning of highly contaminated textiles, *e.g.* carpets or heavy curtains suspected to be treated with PCP (the country of origin may be an indicator) or clothing of workers or other textiles from dioxin-polluted environments.

**Class 2** includes cleaning of uncontaminated clothing and other textiles.

**Table II.8.6 PCDD/PCDF emission factors for source category 8d Dry Cleaning**

8d	Dry Cleaning	Emission Factors (in µg TEQ/t)				Concentration in distillation residue (µg TEQ/t)
		Air	Water	Land	Product	
	<b>Classification</b>					<b>Residue</b>
1	Heavy textiles, PCP-treated, etc.	NA	NA	NA	NA	3,000
2	Normal textiles	NA	NA	NA	NA	50



### Activity rates

As an indication, 15g of residues are formed per kilogram of treated clothes (data from the French Technical Center on Cleaning - CTTN). Activity data can be retrieved from competent authorities that license the dry cleaning shops, and waste collectors.

### Level of confidence

The emission factors for this source category have been assigned a low level of confidence due to changes and complexity in the textile and leather manufacturing.

## 8e Tobacco Smoking

As any other thermal process, “combustion” of cigarettes and cigars produces PCDD/PCDF. The quantity of tobacco in cigarettes varies but is commonly less than 1 gram per cigarette. Cigars vary both in their size and their tobacco load. Large cigars may contain as much tobacco as an entire pack of 20 cigarettes, while small cigars (cigarillos) may be similar in size and tobacco content to that of one cigarette.

### Emission Factors

PCDD/PCDF emission factors for two source classes are listed in Table II.8.7. Revised or newly added emission factors are highlighted in red. Detailed information on how these emission factors have been derived can be found in Annex 52.

### Guidance for classification of sources

**Class 1** should be applied to cigar smoking.

**Class 2** applies to cigarette smoking.

**Table II.8.7 PCDD/PCDF emission factors for source category 8e Tobacco Smoking**

8e	Tobacco Smoking	Emission Factors (µg TEQ/million cigars or cigarettes)				
		Air	Water	Land	Product	Residue
	<b>Classification</b>					
1	Cigar	0.3	NA	NA	NA	<b>0.3</b>
2	Cigarette	0.1	NA	NA	NA	<b>0.1</b>

NB: The emission factors for tobacco smoking are applied to total cigarette/cigar numbers, not to the weight of tobacco.

### Activity rates

The activity rate can be assessed by the following mass-balance equation: Production - Export + Import. While cigarette data are available as numbers of cigarettes, loose tobacco and cigars are usually reported in weight. A conversion factor of 1 g of tobacco per cigarette may be used to estimate the number of cigarettes, *i.e.* 1 ton of loose tobacco is equivalent to 1,000,000 cigarettes.

### Level of confidence

The level of confidence assigned to these emission factors is low due to limited data available and difficult experimental design.

## 9 – Disposal / Landfill

Non-thermal waste disposal processes are addressed in this source group. Except in certain cases, these processes are only routes of PCDD/PCDF release, not sources of PCDD/PCDF formation and release. PCDD/PCDF that are already present in the wastes being treated become concentrated or released to one or more vectors by these treatment and disposal processes (see Table II.9.1).

These processes are used to dispose of PCDD/PCDF-contaminated wastes, many of which are residues of processes that have been addressed in other source groups. The management of these residues, e.g. physical, biological, chemical, or thermal treatment or containment in secure landfills, burial in dumps and pits, spreading on land, or direct discharge of untreated effluents into rivers, lakes or oceans, can result in PCDD/PCDF releases to the environment.

The fate of PCDD/PCDF-containing residues should be well-documented, because of the potential for mismanagement to result in increased and widespread exposure in humans and domestic animals. As an example, the Belgian chicken incident originated in a small volume of used PCB oil (contaminated with PCDF) being introduced into fat subsequently used for producing feedstuff for domestic animals (EU SCAN 2000).

**Table II.9.1 Overview of source categories included in group 9 – Disposal / Landfill**

9 – Disposal / Landfill		Potential release vector				
		Air	Water	Land	Product	Residue
a	Landfills, Waste Dumps and Landfill Mining		x	X		
b	Sewage/sewage treatment	(x)	x	x	x	x
c	Open water dumping		x	X*		
d	Composting			x	x	
e	Waste oil treatment (non-thermal)	x	x	x	x	x

\* Sediment in creeks, rivers, estuaries and oceans.

With relevance to the provisions of Article 5, sources in this category can be classified as follows:

**Table II.9.2 Relevance to Article 5, Annex C of the Stockholm Convention**

No	Toolkit source category	Part II	Part III	Relevant source category in Annex C
9e	Waste oil treatment (non-thermal)		X	Waste oil refineries

An example of elaborating a source inventory and release estimate for this source group is included in the example inventory 10.

### 9a Landfills, Waste Dumps and Landfill Mining

Landfills and waste dumps are sites where waste is buried in engineered landfills and unlined pits or deposited in surface piles (open dumps). An engineered landfill is a constructed waste storage site where the wastes are contained and controlled by liners and caps. In contrast, pits, dumps and piles have no engineered containment or pollution control techniques and are largely unregulated and uncontrolled.

In landfills and dumps, biodegradable wastes decompose with the formation of gases (with methane as a major constituent when the degradation proceeds anaerobically) and leachate. The passage of

rain and other water through the waste in landfills and dumps generates contaminated leachate and runoff. Where no collection systems are installed, landfill gases and leachate escape from the dump in an uncontrolled manner. While PCDD/PCDF have not been quantified/reported in landfill gases, they are known to occur in landfill leachate or seepage and, in some cases, nearby soils.

Combustion of landfill gases in flares and other devices is addressed in source category 3c and releases due to open burning of waste at landfills and dumps are addressed in source category 6b.

### **Landfill mining**

A large amount of PCDD/PCDF and other unintentional POPs have been deposited over the last century in landfills and dumpsites, with the largest reservoirs stemming from chlorine and organochlorine production (see Source Group 10). Landfill mining and reclamation, or excavation/remediation of landfills is a process whereby solid wastes which have previously been landfilled are excavated and processed.

The objectives of landfill mining/reclamation and excavation/remediation can be threefold:

- Recovery of land and landfill space
- Recovery of materials
- Environmental protection and remediation

As an example, PCDD/PCDF contaminated lime has been mined from a landfill containing residues from VCM/EDC production (Torres *et al.* 2012). This contaminated lime was partially used for neutralization of citrus pulp which was subsequently used as feedstuff for cattle in Europe. This resulted in contamination of milk and dairy products in several European countries (Torres *et al.* 2012, Malisch 2000; see example inventory 10).

The excavation of landfills for remediation purposes reduces or prevents releases of more water soluble compounds contaminating groundwater, surface water or drinking water. Excavation can also be undertaken due to long term cost considerations and to avoid burdening future generations.

The quantity of PCDD/PCDF in landfills being excavated is site specific and needs to be individually assessed in each case (Forster 2006, Torres *et al.* 2012, Weber *et al.* 2008). The excavation and remediation activities of landfills containing wastes from organochlorine industries or other wastes highly contaminated with PCDD/PCDF must also consider the risks of occupational exposure to PCDD/PCDF. The excavated wastes need to be treated in an environmentally sound manner as described in the BAT&BEP Guidelines.

### **Emission Factors**

PCDD/PCDF emission factors for three source classes are listed in Table II.9.3. Revised or newly added emission factors are highlighted in red. Detailed information on how these emission factors have been derived can be found in Annex 53.

### **Guidance for classification of sources**

**Class 1** applies to landfills where wastes from source groups 1 to 8 are deposited.

**Class 2** applies to landfilling of waste which may contain some hazardous components. A typical situation is in cases when no waste management is in place.

**Class 3** applies to landfilling of non-hazardous wastes.

When assessing releases from this source category, care should be taken that no double counting occurs. This category covers wastes generated at national level that are landfilled. It does not include municipal or hazardous waste that is accounted for in other source groups or source categories, especially in:

- Source Group 1: 1a Incineration of municipal solid waste, 1b Incineration of hazardous waste and 1c Medical waste incineration;
- Source Group 6: classes 6b1 Fires at waste dumps or 6b3 Open burning of domestic waste;
- Source Group 3: class 4c1 Production of bricks using contaminated fuels or similar high temperature production processes using waste fuels.

**Table II.9.3 PCDD/PCDF emission factors for source category 9a Landfills, Waste Dumps and Landfill Mining**

9a	Landfills and Waste Dumps	Emission Factors (µg TEQ/t waste disposed of)				
		Air	Water	Land	Product	Residue
1	Hazardous wastes	NA	5	NA	NA	NA*
2	Mixed wastes	NA	0.5	NA	NA	50
3	Domestic wastes	NA	0.05	NA	NA	5

\*The residues of wastes from category 1 to 8 are accounted in the respective categories.

### Activity rates

Activity rates might be available on national level and on municipality level. In general there historical data are scarce. Additionally, the set of data for PCDD/PCDF in waste are uncertain because of the small regional coverage of these data.

### Level of Confidence

There are multiple sources of uncertainty associated with the PCDD/PCDF levels in waste and the emissions from landfills. Emission factors are thus assigned a medium to low level of confidence.

## 9b Sewage and Sewage Treatment

Sewage is waste that is dissolved and/or suspended in water. Sewage, also called wastewater, typically includes human feces and urine, bathwater, water used in washing clothes and other items, and, in some cases, storm water run-off and industrial wastewater.

This category addresses municipal sewage that is collected and transported to sewage treatment facilities. Untreated sewage that is collected and discharged directly to surface water, such as rivers, lakes and oceans, is addressed in source category 9c Open Water Dumping. Wastewater and wastewater treatment from industrial production is addressed in Source Group 7 – Production and Use of Chemicals and Consumer Goods.

Sewage treatment ranges from simple removal of large solids by coarse screening to further solids removal in settling ponds, biological and chemical treatment, disinfection, reverse osmosis filtration and other advanced technologies. These commonly used sewage treatment methods produce an aqueous effluent and a solid residue, sewage sludge. PCDD/PCDF concentrations in treated effluent are ordinarily low. However, when chlorine is used to disinfect treated effluent, PCDD/PCDF concentrations can increase, in some cases, by as much as 50-fold (Pujadas *et al.* 2001). Most of the PCDD/PCDF found in sewage and, subsequently, in treated effluent and sewage sludge originate in

other processes or products.<sup>12</sup> For example, PCDD/PCDF may occur in sewage because they have been washed from clothing and other textiles treated with PCDD/PCDF-contaminated biocides or dyes and pigments (see source category 7d), due to the entry into sewers of runoff of atmospheric deposition of PCDD/PCDF from combustion sources (Gahr *et al.* 1991), or due to discharges into sewers of untreated industrial wastewater.

For many years, PCDD/PCDF have been reported in sewage sludge of many countries (Clarke *et al.* 2008). Decreasing trends have been reported in countries such as Germany and Austria, as well as in Spain (Martinez *et al.* 2007, De la Torre *et al.* 2011). The management of sludge can also result in releases of PCDD/PCDF. For example, land application of sludge can lead to increased PCDD/PCDF in soils (Molina *et al.* 2000, Rideout and Teschke 2004), in certain vegetation grown on sludge-treated soils (Engwall and Hjelm 2000), and in the tissues and other products of animals that forage on PCDD/PCDF-contaminated soils (Schuler *et al.* 1997, Rideout and Teschke 2004). Likewise, sludge buried in landfills may contribute to PCDD/PCDF in landfill leachates (De la Torre *et al.* 2011).

Untreated sewage from remote, undeveloped and non-industrialized areas is expected to have relatively low PCDD/PCDF concentrations. Low concentrations may be also expected in countries with stringent controls on discharges of industrial wastewater to sewers, effective controls on the use of PCP, other biocides and dyes and pigments on textiles, and bans on the use of chlorine-bleached toilet paper. Higher levels can be expected in urban areas with mixed industry and use of PCDD/PCDF-contaminated consumer goods. Discharges of untreated industrial wastewater to public sewers can cause very high levels of PCDD/PCDF in sewage sludge (for reference, see Group 7 Production and Use of Chemicals and Consumer Goods).

With more advanced treatment – such as biological and chemical treatment - most PCDD/PCDF are likely to be concentrated in the sludge. The amount of PCDD/PCDF in the effluent is likely to be influenced by the amount of suspended solids remaining in the effluent.

### Emission Factors

PCDD/PCDF emission factors for three source classes are listed in Table II.9.4. Revised or newly added emission factors are highlighted in red. Detailed information on how these emission factors have been derived can be found in Annex 53.

### Guidance for classification of sources

**Class 1** should be applied where, besides normal domestic effluents, industrial effluents with a potential to contain PCDD/PCDF as described for categories 1 to 8 are collected in the same sewer system.

**Class 2** should be applied for urban, industrial areas without specific potential to contain PCDD/PCDF.

**Class 3** should be applied to remote areas with no known PCDD/PCDF sources and urban areas with only domestic inputs.

**Table II.9.4 PCDD/PCDF emission factors for source category 9b Sewage and Sewage Treatment**

9b	Sewage and Sewage Treatment	Emission factors
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<sup>12</sup> Biogenic formation of PCDD/PCDF from dioxin precursors like chlorophenols has been reported in sewage sludge by some authors. However, biological transformation cannot be quantified in terms of emission factors. Since the use of chlorophenol (including PCP) has decreased the last decades, this source can be considered as not relevant. PCDD/PCDF may also be produced where sludge is thermally dried.

Classification		Air	Water (µg TEQ/L)	Land*	Product = Residue (µg TEQ/t d.m.)
1	Mixed domestic and specific industrial inputs**	NA NA	10 <sup>a</sup> 1 <sup>b</sup>		NA <sup>a</sup> 200 <sup>b</sup>
2	Urban and industrial inputs	NA NA	1 <sup>a</sup> 0.2 <sup>b</sup>		NA <sup>a</sup> 20 <sup>b</sup>
3	Domestic inputs	NA NA	0.04 <sup>a</sup> 0.04 <sup>b</sup>		NA <sup>a</sup> 4 <sup>b</sup>

<sup>a</sup>no sludge removal, <sup>b</sup>with sludge removal

\*Use EF<sub>Product</sub> when residue (sludge) is applied to land.

\*\* for those emissions which are not covered in source group 7.

Note: the emission factors are given in pg TEQ/L of treated effluent and in µg TEQ per ton of sewage sludge (dry matter = d.m.) generated.

### Activity rates

Activity rates on production of sewage sludge might be available on national level and on municipality level. One challenge is to assign which facilities to classify as class 1 with specific industrial input. A national survey for PCDD/PCDF in sewage sludge is helpful to facilitate source classification. A regular survey for sewage sludge is not recommended or might be performed every 5 or 10 years. For facilities with elevated levels (above 30 ng TEQ/kg), source(s) might be traced, and measures for release reduction introduced.

### Level of Confidence

The emission factor values are assigned a high confidence level, based on the geographic coverage of available datasets and consistency among the results of the various studies.

## 9c Open Water Dumping

Open water dumping is the practice of discharging untreated wastewater or other wastes directly into surface waters, *i.e.* rivers, ground water, lakes or oceans.

### Emission Factors

PCDD/PCDF emission factors for three source classes are listed in Table II.9.5.

#### Guidance for classification of sources

**Class 1** should be applied if the wastewater being discharged includes both domestic and industrial wastewater with a potential to contain PCDD/PCDF as described for source group 1 to 8 or storm water runoff from urban, peri-urban or industrialized areas.

**Class 2** should be applied for urban and peri-urban areas with little or no industries.

**Class 3** includes remote areas with no known PCDD/PCDF sources.

Table II.9.5 PCDD/PCDF emission factors for source category 9c Open Water Dumping

9c	Open Water Dumping Classification	Emission Factors (µg TEQ/m <sup>3</sup> )				
		Air	Water	Land	Product	Residue

1	Mixed domestic and industrial wastewater	NA	0.005	NA	NA	NA
2	Urban and peri-urban wastewater with little or no industrial input	NA	0.0002	NA	NA	NA
3	Remote environments	NA	0.0001	NA	NA	NA

## 9d Composting

Composting is the biological decomposition of biodegradable solid waste under controlled predominantly aerobic conditions to a state that is sufficiently stable for nuisance-free storage and handling and is satisfactorily matured for safe use in agriculture (Diaz *et al.* 2005). Feedstocks for composting include a wide variety of materials, *e.g.*, kitchen and garden waste, sewage sludge, agricultural crop residues, some industrial wastes, animal manures and human excreta.

PCDD/PCDF values in compost in Europe were between 3 and 12 ng TEQ/kg (Brändli *et al.* 2005, 2008). In Brazil, organic composts (separated at source) had an average PCDD/PCDF content of 14 ng TEQ/kg (Grossi *et al.* 1998). However, composts produced from mixed waste where organic fractions have been separated after collection (“grey compost”) had an average of 57 ng TEQ/kg, with a maximum of 150 ng TEQ/kg in metropolitan areas, and an average of 27 ng TEQ/kg in small towns (Grossi *et al.* 1998). Compost impacted from pulp and paper sludge using Kraft process also had high values (99 ng TEQ/kg). These “grey” composts with levels of 50 ng TEQ/kg and higher are not considered suitable for agriculture or horticulture in Europe. However, standards differ among other regions and countries.

### Emission Factors

PCDD/PCDF emission factors for two source classes are listed in Table II.9.6. Revised or newly added emission factors are highlighted in red. Detailed information on how these emission factors have been derived can be found in Annex 53.

### Guidance for classification of sources

**Class 1** should be applied when the organic fraction is separated from mixed wastes and then composted. Such composts also contain higher levels of heavy metals and plastics.

**Class 2** should be applied for compost where organics (kitchen/market waste, vegetables/fruit etc.) have been separated at source or green materials have been used.

**Table II.9.6 PCDD/PCDF emission factors for source category 9d Composting**

9d	Composting	Emission Factors (µg TEQ/t d.m.)				
		Air	Water	Land*	Product	Residue
	<b>Classification</b>					
1	Compost of organic wastes separated from mixed wastes	NA	NA	NA	<b>50</b>	NA
2	Clean compost (organic wastes separated at source or green material)	NA	NA	NA	<b>5</b>	NA

\*Compost is finally applied to land



### Activity rates

Activity rates on production of compost might be available on national level and on municipality level. The activity rates of composting on household level might not be available from national statistics but might need a survey or an expert judgment.

### Level of Confidence

The emission factor values have been assigned a high level of confidence. Nevertheless, uncertainties exist where organic industrial residues are used (*e.g.* from pulp and paper industry).

## 9e Waste Oil Treatment (Non-thermal)

The estimate of PCDD/PCDF releases from waste oil treatment is difficult for several reasons. Firstly, there is no clear definition of “used” oil or “waste” oil. For the purpose of the Toolkit, waste oils (or used oils) are defined as any petroleum-based, synthetic, or plant- or animal-based oil that has been used. Waste oils may originate from two large sources: used industrial oils, and vegetable or animal waste oils. Among the industrial waste oils, three main oil streams can be identified: industrial oil (for example, hydraulic oil, engine lubricant, cutting oil); garage or workshop oil; and transformer oil. More information can be found in the BAT&BEP Guidelines.

Waste oils have been found to be contaminated with PCDD/PCDF and PCB. PCB-containing oils from transformers are addressed in source category 10f.

At present there is no evidence that PCDD/PCDF or PCB are newly formed in waste oil refineries. The data available indicate that PCDD/PCDF and PCB released from waste oil refineries or waste oil handling and management plants are from the industrial, intentional production of PCB or chlorobenzenes that are present in waste oils either by contamination in the synthesis process (of these chemicals) or have become contaminated during the use phase or earlier recycling processes. More information can be found in the BAT&BEP Guidelines.

Waste oil collected in countries will end up in other processes and has to be included in the categories on waste incineration (1a and 1b), power plants (3a), domestic heating and cooking (3e), cement kilns (4a), brickworks (4c), asphalt mixing stations (4f), or transportation (5d).

The management of PCDD/PCDF or PCB contaminated oil may result in human exposure of the personnel collecting or otherwise handling the oils. During storage and handling, diffuse emissions may occur. Contamination of the environment may also result from spills. Residues from recycling operations may contain high concentrations of PCDD/PCDF. Improper disposal may result in contamination of land or water. It can be assumed that a site- or process-specific evaluation has to be performed.

Presently, no emission factors can be given with respect to any of the release vectors.



## 10 – Contaminated Sites and Hotspots

Article 6 of the Stockholm Convention encourages parties to develop strategies to identify sites contaminated with unintentional POPs. This source group includes an indicative list of activities that might have resulted in the contamination of soils and sediments with PCDD/PCDF and other unintentional POPs, including related deposits.

PCDD/PCDF from reservoirs including contaminated sites and hotspots represent nowadays an important source of human exposure, often through food contamination: recent accidents involving food and animal feedstuff in Europe have been caused by historic PCDD/PCDF contamination from past production of chlorinated organics and contaminated sites (Fiedler *et al.* 2000b, Torres *et al.* 2012, Weber *et al.* 2008a,b) highlighting that PCDD/PCDF are released from these sources into the food chain.

The procedure comprises three tasks:

- I. Identifying historical activities that could have caused contamination and identifying the potentially contaminated sites;
- II. Assessing these sites for the likely magnitude of the contamination and ranking by their exposure risk;
- III. Assessing the degree of contamination of the most significant sites by detailed analysis.

### Steps for identification, ranking and detailed assessment of the sites

#### I. Identifying potentially contaminated sites

A wide variety of PCDD/PCDF sources exists worldwide, which has likely resulted in a large number of (potentially) contaminated sites through historic releases. The Toolkit shows that the strength of the various PCDD/PCDF sources varies by several orders of magnitude. Therefore, a prioritization of contaminated sites from historic sources needs to consider the total amount of PCDD/PCDF that was likely produced from the respective sources, the related management schemes and former destruction efforts. Often, details on the management of historic releases are not known, therefore a tiered approach is needed to inventory and categorize sites.

The largest amounts of PCDD/PCDF and other unintentional POPs were generated in the production processes of organochlorine chemicals, in particular of PCDD/PCDF precursors such as chlorophenols, PCB or other chlorinated aromatic compounds. Tens to hundreds of kg TEQ of historic deposits have been documented for single factories (Götz *et al.* 2012, Verta *et al.* 2010, Forter 2006); amounts of the same order of magnitude were recorded for single hotspot sites (Götz *et al.* 2012). The same is true for unintentionally produced HCB, where single factories have disposed of HCB wastes in the order of 10,000 tons (Weber *et al.* 2011b, Vijgen *et al.* 2011).

The following source groups should be considered when setting priorities for establishing inventories and assessing sites potentially contaminated with PCDD/PCDF and other unintentional POPs, as well as (historic) stockpiles of contaminated wastes<sup>13</sup>:

- Production of chlorine (in particular chlor-alkali processes having used graphite electrodes).

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<sup>13</sup> The list is established according to the life cycle of chlorine and organochlorine compounds.

- Production sites of PCDD/PCDF precursors (*e.g.* chlorophenols, chlorinated pesticides, PCB) or HCB precursors (*e.g.* perchlorethene, trichloroethene, tetrachlormethane) and related waste deposits.
- Factories having used elemental chlorine in production processes (*e.g.* magnesium production, or pulp and paper production) with high PCDD/PCDF releases often in solids/sludges or to water, including related contaminated sediments.
- Use or application sites of organochlorine compounds known to contain PCDD/PCDF or having PCDD/PCDF precursor potential (production sites of PCB-filled equipment, PCP use in wood preservation, application areas of pesticides containing PCDD/PCDF).
- End-of-life storage and disposal/dumping sites of organochlorine compounds known to contain PCDD/PCDF or having PCDD/PCDF precursor potential (obsolete pesticide storage/burial, PCB storage).
- Thermal sources with high historic releases of PCDD/PCDF to air, water or wastes and related contamination.
- Accidents including fires with liquids and other materials polluted with PCDD/PCDF (often taking place at sources mentioned above).

Monitoring data are rarely available before the development of an inventory. A listing of contaminated sites is therefore prepared based only on information on historic activities having likely resulted in high releases of PCDD/PCDF and other unintentional POPs over the last century. Consequently, in the initial stage of inventory development, the sites related to the above listed high priority activities can be categorized without a detailed assessment as “potentially polluted sites”. Using this simple approach (Tier 1), a wide range of “potentially polluted sites” can initially be listed. Often, in this stage, only the factories and areas surrounding the known or suspected sources can be identified as “potentially polluted”, without knowing details on *e.g.* deposits, polluted soil or sediments. These sites will be included in a list or a database of contaminated sites, noting that further investigations are needed.

## **II. Ranking the contaminated sites**

In the second phase (Tier 2), these “potentially polluted sites” are subject to further assessment of historic production, and evaluation of quantities of chemicals produced, waste generation and management, thermal processes used for destruction or releases and historic release vectors. In this tier 2 assessment, the detailed location of potentially contaminated sites is assessed, in particular production sites, related landfills and dump sites, rivers and lakes having received releases, and areas where air releases have been deposited. These sites can be identified as “likely contaminated sites” or “contaminated sites”, depending on PCDD/PCDF contamination levels. Such data might be documented in archives of the respective companies or competent authorities responsible for factory inspection/audits. In addition, data from factories with similar production or technologies may be used for a first semi-quantitative estimate. Tier 2 might already include a first screening of PCDD/PCDF contamination at suspected sites with high human exposure risk to assess/confirm PCDD/PCDF pollution and facilitate appropriate action. Based on the compilation of this information, the site can be listed in the inventory as a (likely) polluted site, and the need for a further detailed assessment should be noted. Already at this stage, the site might be classified as a high priority site or as a site with lower priority. Depending on the priority classification, the respective competent

authority and the owner of the site are informed of the necessary steps for further detailed assessment of pollution (Tier 3) and the urgency of such assessment. A preliminary risk assessment for each site/hotspot should be made in order to establish the necessary national priorities, so that in case of limited available budgets, the most urgent sites can be selected and dealt with accordingly.

### **III. Detailed assessment of the most significant contaminated sites**

In the third phase (Tier 3), a detailed assessment of the site is conducted including field measurements to assess the extent of contamination in soils, sediments and possibly ground and surface water (for the more water-soluble unintentional POPs). This assessment also includes an evaluation of potential releases and human exposure via all relevant pathways. Detailed records of the location of the sites should be compiled *e.g.* places where the potentially contaminating operations took place and where associated wastes have been disposed of, ideally using geospatial data. The current use of the site and any associated human exposure risks should also be assessed and recorded. A detailed risk assessment and a conceptual site model might also be developed at this stage.

Details on assessing POPs contaminated sites have been compiled in the following documents and are not further described:

- a) UNIDO “*POP contaminated site investigation and management toolkit*”, which aims at assisting developing countries in the identification, classification and prioritization of POPs-contaminated sites (<http://www.unido.org/index.php?id=1001169>). The report can be downloaded from the internet.<sup>14</sup>
- b) World Bank “*The Persistent Organic Pollutants (POPs) Toolkit*”, which provides training modules and interactive tools for risk-based approaches to prioritize and manage POPs-contaminated sites and other hazardous substances (<http://www.popstoolkit.com/>).

A series of practical examples and best practice cases of PCDD/PCDF inventories for the most relevant source categories is included in the example inventory 11 including, where available, quantitative PCDD/PCDF data.

It is important to note that polluted sites, in particular at larger chemical production sites, are often impacted by a range of pollutants; contamination with PCDD/PCDF and other unintentional POPs may be coupled with pollution by other organohalogen compounds or heavy metals, which would also be included in the assessment of the site. For instance, chlor-alkali processes having used mercury technology have often resulted in a combination of mercury, PCDD/PCDF, PAH and other heavy metal contamination (Otto *et al.* 2006). All these aspects should be taken into account in the identification and inventory process of polluted sites.

The identification and inventory of polluted sites is merely a first step to manage related risks and for final cleanup and rehabilitation. A certain system of polluted sites management should thus be set up.

### **Polluted sites databases and registers**

The inventory data should finally be integrated in a national database of contaminated sites. Taking into account the multi-pollutant nature of many contaminated sites, it is both practical and economic

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<sup>14</sup>[http://www.unido.org/fileadmin/user\\_media/Services/Environmental\\_Management/Stockholm\\_Convention/POPs/toolkit/Contaminated%20site.pdf](http://www.unido.org/fileadmin/user_media/Services/Environmental_Management/Stockholm_Convention/POPs/toolkit/Contaminated%20site.pdf)

to maintain a single national database for all contaminated sites, with information on the types of pollutants for the respective sites, including PCDD/PCDF, PCB and possibly other POPs.

Such national databases of contaminated sites have been developed over the last three decades in certain countries. For example, the United States Superfund program<sup>15</sup> is based on such a national inventory compilation of contaminated sites (see example inventory for source category 10I). Canada has a federal contaminated sites inventory which is publicly available, including PCDD/PCDF and PCB as listed pollutants.<sup>16</sup> Some countries have developed and published transparent guidelines to develop such inventories *e.g.* the Swedish EPA (Swedish EPA 2002).

Specific global or regional contaminated sites databases have also been established *e.g.* by the Blacksmith Institute ([www.worstpolluted.org](http://www.worstpolluted.org)), Robin des Bois organization ([www.robindesbois.org](http://www.robindesbois.org)), the HCH and Pesticide Association ([www.ihpa.info](http://www.ihpa.info)) (Vijgen *et al.* 2011).

The development of such inventories of contaminated sites can be framed by legislation requiring their establishment for the protection of future generation, and/or protection and management of soils and water resources. The European Commission has established such a requirement in the proposal of a soil framework directive (EC 2006).<sup>17</sup>

If a country already has a national database of contaminated sites, the information gathered via inventories of sites contaminated with PCDD/PCDF and other unintentional POPs will be added to the existing database. If such a database does not exist in a country, the establishment of a contaminated site inventory can initiate the development of a national contaminated sites inventory database.

Using the three phase approach the different categories and sites within the categories can be ranked and assessed according the priority setting based on risks. These assessments are also included in the contaminated sites inventory database.

## **10a Production Sites of Chlorine**

Certain processes for the manufacture of chlorine have been associated with high formation and releases of PCDD/PCDF and other unintentional POPs (Weber *et al.* 2008). In addition to well-documented releases from the chlor-alkali process (Otto *et al.* 2006), earlier chlorine production using the Weldon or Deacon process has also resulted in PCDD/PCDF contaminated sites (Balzer *et al.* 2007, 2008).

### **I. Chlor-alkali production**

The manufacture of chlorine using graphite anodes generates PCDD/PCDF contamination of the residues. Contamination levels close to 4 mg TEQ/kg in chlor-alkali residues have been reported; contaminated soil samples ranged from 0.15 µg I-TEQ/kg to 23.1 µg I-TEQ/kg (She and Hagenmaier 1994, Otto *et al.* 2006). The only chlor-alkali production site for which a PCDD/PCDF inventory has been published was operated in Rheinfelden/Germany. The deposited residues and contaminated soils were estimated to contain a total of 8.5 kg I-TEQ PCDD/PCDF from residues of the chlor-alkali process (see example 10aI).

Chlorine was produced almost exclusively using graphite anodes until it was gradually replaced by metal anodes and other technologies starting with the 1970s. The graphite residue was highly

<sup>15</sup> <http://www.epa.gov/superfund>

<sup>16</sup> <http://www.tbs-sct.gc.ca/fcsi-rscf/home-accueil-eng.aspx>

<sup>17</sup> COM(2006)232, [http://ec.europa.eu/environment/soil/three\\_en.htm](http://ec.europa.eu/environment/soil/three_en.htm)

contaminated with PCDF, PCN and other chlorinated PAHs mainly from the reaction between chlorine and the pitch binder (Takasuga *et al.* 2009). In developing regions, graphite anodes have been used until recently and might possibly still be in use.

Primary locations for contamination from these operations include soil and, if leaching has occurred, neighbouring compartments and eventually sediments of nearby rivers. High concentrations of mercury could be an indicator for contamination with PCDD/PCDF as well. Barium levels in the deposited chlor-alkali residues were also found to be a useful and inexpensive monitoring parameter for tracking contamination of residues and deposits. This approach has been used for screening and mapping a German site impacted by widespread chlor-alkali residues (Otto *et al.* 2006; see example 10a).

## **II. Leblanc process and associated chlorine/bleach production**

High concentrations of PCDF (and minor concentrations of PCDD) were formed by Leblanc Soda and associated processes. PCDD/PCDF levels of up to 500 µg TEQ/kg have been reported in deposits from a former German Leblanc factory (Balzer *et al.* 2007, 2008; see example 10a). The Leblanc process was extensively used until early 20th century to produce sal soda/sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) from sodium chloride (NaCl). The waste from this process (HCl) was recycled in some facilities by oxidation to produce chlorine/calcium hypochlorite (bleaching powder) either via manganese oxide (Weldon process) or by CuCl<sub>2</sub> catalysts (Deacon process) (Weber *et al.* 2008, Encyclopaedia Britannica 1911). The major source of PCDD/PCDF precursors was coal tar which was used as a filler and surface protection material. In addition to PCDD/PCDF, other unintentional POPs and chlorinated aromatic compounds were formed (Takasuga *et al.* 2009, Bogdal *et al.* 2008).

Leblanc factories were predominantly operated in the UK, France and Germany with a few facilities in other European countries (Balzer *et al.* 2008; see example 10a). For inventories of former Leblanc factory sites, it is important to assess if the factory recycled HCl to chlorine/bleach, as recycling would be associated with high PCDD/PCDF levels in the wastes and likely contamination of the land where these wastes were deposited. In addition, PCDD/PCDF contamination has been found in areas where Leblanc ovens have been operated and since demolished (Balzer *et al.* 2008).

### **10b Production Sites of Chlorinated Organics**

The largest PCDD/PCDF contaminated sites and hotspots have been generated by the production and application of chlorinated organics. For some production processes, other unintentional POPs were/are major residues. Furthermore, considerable quantities of product, either remaining in the residues or as faulty batches, were deposited on or close to the production sites. A prime example is lindane/HCHs, with only approximately 15% of the total mass emerging as product, and the remaining 85% representing HCH waste isomers, dumped in the vicinity of the production facilities. The production of DDT and endosulfan also generate large amounts of wastes containing POPs which have often been landfilled. Wastes from the organochlorine industry are now destroyed in BAT/BEP incinerators in developed regions. However, these wastes were often landfilled or dumped until the 1970s/1980s. In developing regions, such wastes might still be landfilled nowadays.

The inventory of such production sites and related contaminated sites should consider:

- The former and current production portfolio should be assessed for chemicals containing or possibly containing PCDD/PCDF, HCB or other unintentional POPs (see Annex 2 and example 10b). The highest concentrations of PCDD/PCDF are expected to be associated with the

production of chlorinated phenols, their derivatives, and other chlorinated aromatic compounds. However the production of non-aromatic chemicals like chlorinated solvents has also generated wastes containing unintentional POPs *e.g.* 10,000 tons of unintentionally produced HCB from single production sites (Weber *et al.* 2011).

- Former and current management practices for waste residues should be reviewed and an inventory of related production sites, stockpiles and landfills should be developed (see examples 10bII and 10bIII).
- Contamination with PCDD/PCDF of buildings and soil is likely to be found at current or former production sites of chlorinated organics.
- If wastewater was discharged into receiving waters, sediments and floodplains of entire river systems or bays can be contaminated (see example 10bI).
- If wastewater has been allowed to settle in ponds, sediment or sludge from these settling ponds can contain high concentrations of PCDD/PCDF.

### **I. Production sites of chlorophenol**

High concentrations of PCDD/PCDF can be expected at sites where chlorinated phenols were produced. In the case of Times Beach, USA, where production residues were spread, contaminated soils have been reported as having concentrations of up to 33,000,000 ng TEQ/kg (Rappe 1984). Levels around factories can be as high as 200,000 ng TEQ/kg (di Domenico *et al.* 1982). Where production residues have been released via water discharge, sediments can be polluted with tens of kg TEQ (Verta *et al.* 2008; see example 10bI). PCDD/PCDF in related deposits are reported to total 7.7 kg TEQ for a PCP production facility in Germany (Otto *et al.* 2006; see example 10bI) and 22.3 kg from a 2,4,5-T production site also located in Germany (Götz *et al.* 2012).

### **II. Former lindane production where HCH waste isomers have been recycled**

In the production of lindane (gamma-HCH), approximately 85% HCH waste isomers are formed in the chlorination step of benzene as unintentional POPs (Vijgen *et al.* 2011). The active gamma-isomer used to be separated and the remaining 85 to 90% waste isomers, consisting mainly of alpha-HCH and some beta, delta and epsilon-HCH, were dumped. This practice has generated the largest international POPs stockpile, estimated at 4 to 7 million tons, often dumped in the vicinity of the factories (Vijgen 2006a,b, Vijgen *et al.* 2011). To avoid such dumping, waste isomers have been recycled at some production sites (Vijgen *et al.* 2011; see example 10bII). Recycling of HCH by thermal decomposition to produce technical tri/tetrachlorobenzene generated highly contaminated residues containing 1.4 to 13% PCDD/PCDF with I-TEQ in the high ppm range (90 to 610 ppm) (Vijgen *et al.* 2011, Zheng *et al.* 1999). The total PCDD/PCDF amount in registered waste disposed of by a German factory was estimated to be between 333 and 854 kg PCDD/PCDF I-TEQ (53 -102 tons total PCDD/PCDF) (Götz *et al.* 2012; see example 10bII). Since the recycling of HCH waste has been carried out at several lindane production sites, related contamination can also be expected at these sites (Vijgen *et al.* 2011).

### **III. (Former) production sites of other chemicals known or suspected to contain PCDD/PCDF or other unintentional POPs**

A wide range of production residues from organochlorine chemicals can be considered to be contaminated with PCDD/PCDF or other unintentional POPs (see Annex 2). Some data may be



available for levels in products (see Source Group 7), however data on levels of PCDD/PCDF or other unintentional POPs in the residues have not been published. Emission factors for most residues are currently not available and will depend on the specific technologies used. Detailed data for the inventory need to be generated for the individual sites including information on the (former) products and intermediates and the respective management and disposal procedures. These production sites and related deposits can be inventoried as potentially contaminated with PCDD/PCDF, noting that “further assessment is necessary”. As an example, an inventory has been compiled for the production wastes generated and landfilled by the Basel Chemical Industry (see example 10bIII).

#### **IV. Production sites of chlorinated solvents and other “HCB waste”**

In the production of certain solvents (*e.g.* carbon tetrachloride, tetrachloroethene, trichlorobenzenes, trichloroethene, trichlorotoluenes), large amount of wastes containing HCB as a prime contaminant (“HCB waste”) are generated (Jacoff *et al.* 1986, Jones *et al.* 2005). For one facility, an emission factor of 1.8% was calculated on the basis of the solvents produced (see example 10bIV; Weber *et al.* 2011b). Other studies have estimated that 4% of “HCB waste” is generated from tetrachloroethene production. For some solvent production, it is reported that individual factories have deposited or stored some 10,000 tons HCB waste (Weber *et al.* 2011a,b). Some of these wastes also contained relevant levels of PeCB (see example 10bIV).

For an inventory of deposits and dumps from solvent production, the following steps are recommended:

- Establish the total quantities of organochlorine solvent produced at the site.
- Establish whether specific factors for factory-generated wastes or data on the total deposited wastes are available. Otherwise a factor of 2% “HCB waste” for the solvents mentioned above can be used.
- Assess the waste management practices over time *i.e.* the time over which the wastes have been deposited, when improved treatment/destruction capacity for production residues was added.
- Map and assess the deposits, associated contamination and related risks.

HCB is also the prime unintentional POP contaminant in the production of certain pesticides (*e.g.* PCNB, PCP, dacthal, daconil, hexachlorocyclopentadiene) (Jacoff *et al.* 1986) and of tetrachlorophthalic acid and related dyes such as chlorinated phthalocyanines (Government of Japan 2007). A similar approach to the assessment of “HCB waste” from solvents can be used for these sites.

#### **V. (Former) PCB and PCB-containing materials/equipment production**

PCB and PCB-containing materials (varnish/paints, sealants, etc.) were produced at chemical plants, and PCB-containing equipment at electrotechnical plants. According to Fedorov (2003) and Ishankulov (2008), annual releases of PCB into the environment from production processes of PCB-containing capacitors at the Ust-Kamenogorsk plant in Kazakhstan generated some 188-227 tons PCB (10-12% of the total PCB used). These releases lead to significant environmental contamination with PCB and PCDD/PCDF, in particular at production sites. These sites can thus be treated as potential hotspots. In addition, storage sites of solid waste and sewage sludge from such facilities are also potential hotspots.

The procedure for revealing such hotspots includes the steps described below:

- A compilation of a list of enterprises where PCB and PCB-containing materials/equipment have been produced;
- Collection of general information about the enterprises (location, the area occupied by the plant, production timeframe, volume of PCB production or PCB used, volume of PCB-containing waste, waste water and sewage sludge, emissions via these vectors, etc);
- Localization of dumps of PCB-containing waste and sewage sludge storage;
- Collect information on PCB leakages, monitoring of POPs content in the environment, etc;
- Estimation of PCDD/PCDF discharges into the environment based on PCB leakages data.

### **10c Application Sites of PCDD/PCDF Containing Pesticides and Chemicals**

These sites include locations where pesticides and other chemicals containing PCDD/PCDF have been applied. Dioxin-containing herbicides/pesticides such as 2,4,5-T, 2,4-D, PCP or others have been applied in agriculture or for clearing vegetation. In Vietnam, spraying of the defoliant Agent Orange and other 2,4,5-T/2,4-D containing agents during 1963-1970 caused extensive environmental contamination and human exposure (Schechter 1994, Allen 2004) releasing some 366 kg TEQ (Stellmann *et al.* 2003). A comprehensive inventory for historic agricultural pesticide use (mainly PCP and CNP) has been established for Japan and is estimated at 460 kg TEQ, having migrated partly from agricultural fields to river sediments and sea (see example 10c). The human milk contamination measured in Japan today is correlated to former pesticide use (Tawara *et al.* 2006, Weber *et al.* 2008).

The use of other organochlorine chemicals having resulted in large contaminated sites are *e.g.* solvents such as tetrachloethene or trichlorethene, which can be contaminated with HCB and PeCB.

For establishing a country inventory, either own PCDD/PCDF data measured from historic pesticides and other chemicals, or emission factors established by other studies might be used (see example 10c). The impacted areas and nearby river systems should be included in the inventory. PCDD/PCDF levels in grazing animals and milk, or in fish in the affected water systems might be assessed.

### **10d Timber Manufacture and Treatment Sites**

Saw mills and timber manufacturing sites are often associated with the use of pentachlorophenol. Soils and sediments can be contaminated with PCDD/PCDF as these industries use large volumes of water and are often located close to rivers. The application of PCP in Sweden, for example, has released between 5 and 50 kg TEQ on these sites, and a further 200 kg TEQ in the product (Swedish Environmental Protection Agency 2005). As PCP and PCP-Na have a much higher water solubility and shorter half-lives, the concentration of PCP in soils or sediments can only give approximate indications of PCDD/PCDF contamination.

Inventories can be established using former application quantities and contamination levels. In addition to an inventory of PCP application sites, a rough inventory of former PCP use and related PCDD/PCDF in treated wood might be established.



## 10e Textile and Leather Factories

PCDD/PCDF and other unintentional POPs containing chemicals like PCP, chloranil and certain dyes have been, and sometimes still are, used in this sector. Contaminated sites or hotspots can be expected at production sites where these chemicals have been stored, used and discharged. In particular, adjacent sediments and waste deposits are likely to be contaminated. Areas where sludges from production or from wastewater treatment have been applied can also be contaminated and should be included in the inventory.

## 10f Use of PCB

The use of PCB has generated a large number of sites and hotspots contaminated with PCDF and dioxin-like PCB via production, use in industries, releases from equipment and open applications (see examples 10fI and 10fII). Commercial mixtures of PCB contain dioxin-like PCB, non-dioxin-like PCB and PCDF, with a major TEQ contribution (> 90%) from dioxin-like PCB (Takasuga *et al.* 2005). PCDF releases can only be estimated based on of the amount of PCB leaked. For this assessment, the total TEQ of PCDF and dioxin-like PCB needs to be considered. With the increasing age of the equipment and longer time of operation, PCDF concentrations in equipment fillings increase, and in the case of high thermal stress (fire event, short circuit) PCDF become the main TEQ contributor.

About 60% of the total volume of PCB was used as dielectric fluids in transformers and power capacitors globally (Breivik *et al.* 2007, Willis 2000). The open uses of PCB, largely as sealants and paints in buildings and in industrial installations, can be considered as hotspots.

If the transformers and capacitors are in a good condition and well maintained, with no leakage, PCB and PCDF are not released into the environment. Once the equipment is leaking, PCDF together with PCB and possibly PeCB will subsequently be released into the surroundings, in soils and sediments. PCB can serve as an indicator for PCDF contamination.

Sites with PCB-containing equipment in use or storage should be treated as potential hotspots. The number of such sites per country may be rather large (see example 10fI; Kukharchyk and Kakareka 2008).

The main tasks for inventorying PCB-contaminated sites and hotspots are:

- Identification/localization of sites where PCB-containing transformers and capacitors are in use or stored, including damaged equipment and PCB waste and sites of open PCB application;
- Identification of PCB leakage;
- Development of the hotspot list;
- Assessment of volumes of PCB leakage and releases of PCDD/PCDF.
- Assessment of PCDD/PCDF concentrations in
  - o PCB transformers/capacitors from producers where PCDF levels are currently unknown;
  - o Sites where transformer fires, short circuits or other fires involving PCB have occurred.

The identification and assessment can be performed based on a tiered approach as presented below.

## 1. Baseline approach

The basis for hotspots accounting is the national inventory of PCB according to Annex A, Part II of the Stockholm Convention. All sites where PCB-containing equipment can be found in use or storage are treated as hotspots. The baseline approach allows the assessment of the total number of potential hotspots, total volumes of PCB and PCDD/PCDF in PCB-containing equipment, as well as potential leakages of PCB and PCDD/PCDF into the environment, using the results of the national PCB inventory.

To differentiate between lower and higher chlorinated PCB congeners, as needed for estimating PCDD/PCDF releases, it can generally be assumed that capacitors are filled with lower chlorinated PCB, while transformers include higher chlorinated PCB with associated PCDD/PCDF levels (Table II.10.1).

For a preliminary assessment of PCB releases into the environment, emission factors given in the EMEP/EEA Atmospheric Emission Inventory Guidebook (2009) may be used (Table II.10.1). Using data on the volumes of lower and higher chlorinated PCB and PCDD/PCDF content in PCB liquids (Table II.10.2), it is possible to estimate PCDD/PCDF and dioxin-like PCB content in PCB equipment and their environmental releases.

**Table II.10.1 PCB release factors from electrical equipment**

10f	PCB Filled Transformers and Capacitors	PCB release (kg/t dielectric fluid)	Country or region
1	Transformers	0.06	Europe
		0.3	North America
		0.3	CIS countries
2	Capacitors	1.6	Europe
		4.2	North America
		2.0	CIS countries

**Table II.10.2 Concentrations of PCDD/PCDF and dioxin-like PCB in unused commercial PCB**

PCB type	PCDD/PCDF in unused commercial PCB (µg TEQ/t product)	Dioxin-like PCB (µg TEQ/t product)*
Low chlorinated, e.g., Clophen A30, Aroclor 1242	7,000 – 15,000	1,900,000-3,500,000
Medium chlorinated, e.g., Clophen A40, Aroclor 1248; KC-400; KC-500	23,000 – 70,000	12,000,000-16,000,000
Medium chlorinated, e.g., Clophen A50, Aroclor 1254	300,000	12,000,000-16,000,000
KC-600; KC-1000	22,000	4,100,000 - 10,000,000
High chlorinated, e.g., Clophen A60, Aroclor 1260	1,500,000	4,100,000 - 10,000,000

\*Data for dioxin-like TEQ in low, medium and high chlorinated PCB are derived from PCB mixtures (Takasuga *et al.* 2005).

If the results of the PCB inventory contain detailed PCB data per site and a clear indication of sites, the list of potential hotspots should be compiled. It should contain the details of the location, coordinates, facility name, type and number of PCB-containing equipment, volume of PCB and the state of the equipment. This list can then serve as a basis for further investigation of hotspots.

## **2. Detailed approach**

The detailed approach is used when the results of the national PCB inventory are partial, inaccurate or not applicable for the identification of hotspots. In such cases, additional questionnaires are sent to governmental bodies, state offices or directly to facilities which hold or operate PCB-containing equipment. In addition to usual questions on the number of PCB-filled equipment, the questionnaires should also enquire on PCB leaks, accidents involving such equipment, description of sites with PCB, results of analysis of PCB in soils and water etc.

## **3. Comprehensive approach**

Through the comprehensive approach, in addition to the results of the national PCB inventory and/or questionnaires to owners of PCB-filled equipment, special investigations of PCB-filled equipment or storage sites are organised, including on-site inspection, soil and other media sampling and analysis, estimation of polluted areas, volumes of leakages, PCB stocks in soil, depth of pollution, risk assessment etc. During the first stages, priority should be given to sites with the largest stocks of PCB-filled equipment, sites with accidents and significant leakages and sites with the highest risk of water and soil pollution.

The results of such a comprehensive inventory allow the preparation of a detailed register of hotspots, with the indication of their prioritisation for remediation measures.

As for the presentation of results of the hotspot inventory (applying the baseline and detailed approach), these can be included in the relevant Excel file (in Source Group 10); the number of identified hotspots, volumes of PCB in equipment (and distribution between lower and higher chlorinated congeners) are needed as input to estimate PCDD/PCDF releases from these sources. For the comprehensive inventory, separate reports are prepared.

## **10g Use of Chlorine for Production of Metals and Inorganic Chemicals**

In addition to organochlorine industry, chlorine was/is used in a range of other industries, resulting in PCDD/PCDF containing residues and releases. For example, pulp and paper sludge from bleach process using elemental chlorine have been highly contaminated with PCDD/PCDF and other chlorinated compounds. The application of such sludges to land or through dumping of sludges resulted in hotspots or contaminated land (see example 10g).

Elemental chlorine either remains in the final product (*e.g.* HCl, NaOCl, ClO<sub>2</sub>, phosphorous chlorides or metal chlorides) or is simply used in the process (*e.g.* titanium dioxide, magnesium or silicon) (Stringer and Johnston 2001). For some of these processes, high PCDD/PCDF formation and release potential has been documented. Contaminated sites have been assessed worldwide, *e.g.* magnesium production in Norway which polluted several fjords and associated food webs with an estimated total PCDD/PCDF release between 50 and 100 kg TEQ (Knutzen and Oehme 1989). The production of titanium dioxide using chlorine process can also generate PCDD/PCDF in the order of kg/year (Wenborn *et al.* 1999).

For an inventory of contaminated sites from processes using chlorine *e.g.* production of pulp and paper, magnesium production, TiO<sub>2</sub>, former releases of these productions, impacted sediments and deposits of residues should be considered.

## **10h Waste Incinerators**

Emissions from non-BAT incinerators can result in the contamination of milk, eggs or vegetables in the surroundings of incinerators (Liem *et al.* 1991, Schmid *et al.* 2003, DiGangi and Petrlik 2005, Watson 2001). In particular, non-BAT incinerators that process organochlorine products, especially PCDD/PCDF precursors (PCB, chlorophenols, chlorobenzenes and other chlorinated aromatics), can result in high emissions of PCDD/PCDFs with considerable impacts on the local environment (Holmes *et al.* 1994, 1998). Only a limited number of cases of PCDD/PCDF contaminated sites from waste incinerators have been documented to date, showing that release vectors from incinerators - air, solids and water - can lead to PCDD/PCDF contaminated sites if not appropriately managed and controlled (see example 10h). The areas around incinerators can also be contaminated from spills of hazardous chemicals treated/destroyed in these facilities.

For the inventory of PCDD/PCDF contaminated sites from incinerators (and other thermal facilities), (former) management practices and disposal of ashes (in particular fly ash and APC residues) and water release from wet scrubbers<sup>18</sup> should be assessed. Contaminated sites via deposition from air releases are only expected for non-BAT incinerators which emit high PCDD/PCDF levels over extended time periods. In addition to soil measurements, PCDD/PCDF levels in eggs or cow's milk in the vicinity of the incinerator are potentially good indicators of the contamination status.

## **10i Metal Industries**

A limited number of PCDD/PCDF contaminated sites associated with metal industries have been documented. Typically, toxic heavy metals represent the key contaminants for sites associated with these industries, while PCDD/PCDF are generally regarded as minor by-products.

Releases from primary metal production processes can cause PCDD/PCDF contaminated sites via distribution of metal industry slag, as recorded in Germany. In this case, more than 400,000 tons of slag from a specific primary copper production process, which was highly contaminated with PCDD/PCDF (10,000 to 100,000 ng TEQ/kg), was used as a surface cover for more than 1,000 sports fields, playgrounds and pavements in Germany and neighbouring countries (Ballschmiter and Bacher 1996, Theisen *et al.* 1993). PCDD/PCDF contaminated sites around a sinter plant in Italy have also resulted in restrictions on grazing (Diletti *et al.* 2009). Emissions from a secondary copper smelter in Rastatt/Germany contaminated surrounding soils, including residential areas, with PCDD/PCDF levels above the German limit values for contaminated soils (Hagenmaier *et al.* 1992).

For the inventory of PCDD/PCDF (and heavy metal) hotspots and contaminated sites, the air releases over years/decades should be considered as well as the management and disposal of ashes.

## **10j Fire Accidents**

Fires can produce soot and residues with elevated concentrations of PCDD/PCDF (see also category 6b). High levels of contamination result from fires where chlorinated aromatic compounds are burned such as PCB transformer fires or fires of pesticide stocks or other organochlorine stockpiles.

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<sup>18</sup> According to BAT, wet scrubbers operate in closed cycles with phase out of the salt and appropriate deposition.

Fires in buildings with concentrated amounts of flame retarded material or high level of PVC can also result in high PCDD/PCDF releases and deposition, normally concentrated in the soot (see example 10j). The soot should thus be collected and disposed of properly as hazardous waste.

### **10k Dredging of Sediments and Contaminated Flood Plains**

Sediments from harbours or downstream of industrial discharge pipelines from any of the above-listed industrial activities can be contaminated with PCDD/PCDF, HCB and other pollutants like heavy metals. Very often, to maintain access through channels, these sediments are dredged and deposited on land. This activity only removes PCDD/PCDF contamination from its location and from the aquatic environment, and transfers the same level of contamination to another location with potentially new exposures. When inventories of dredging activities are established, the deposition of sediments on areas used for agriculture and residential housing should be highlighted and possibly assessed for levels of contamination.

Rivers with a history of PCDD/PCDF contamination can have PCDD/PCDF contaminated floodplains in addition to polluted sediments. Since floodplains are often used for grazing or in agriculture, the inventory and management of impacted floodplains should be performed to prevent human exposure (see example 10k).

### **10l Dumps of Wastes/Residues from Source Groups 1-9**

Where PCDD/PCDF containing products or residues have been disposed of, there is a probability that these contaminants will be released into the environment. PCDD/PCDF are relatively immobile in dumps or landfills as long as there are no organic co-deposits facilitating leaching or seepage water capable of mobilizing the contamination. Of particular importance is the remobilization of PCDD/PCDF-containing deposits if such landfills or dumps are excavated due to remediation measures or for mining purposes (see category 9a; see example 10l).

Chemical or otherwise hazardous landfills containing PCDD/PCDF are sometimes secured by engineering measures. Because of their persistence, PCDD/PCDF and other unintentional POPs will persist in landfills for many decades or centuries (Balzer *et al.* 2008). Over these extended time frames, engineered landfill systems, including liners, gas and leachate collection systems will inevitably degrade and lose their structural integrity and capability to contain persistent contaminants (Allen 2001, Weber *et al.* 2011a).

Landfills and deposits should thus be inventoried and included in a database. In a systematic inventory of landfills/dumps within a country, the specific presence of PCDD/PCDF and other unintentional POPs should be included.

### **10m Kaolin or Ball Clay Sites**

Ball clay and kaolinic clays in different regions in the world can contain PCDD/PCDF with a specific OCDD dominated pattern (Ferrario *et al.* 2007, Horii *et al.* 2011). A first global inventory has been established by Horii *et al.* (2011). Typical for all samples is the almost total absence of PCDF, and the nearly identical congener/isomer distribution throughout all geographies. Thus, PCDD appear to have been formed by natural processes possibly millions of years ago (Ferrario *et al.* 2007, Horii *et al.* 2011). Kaolin samples from Africa have also been found to contain elevated levels of PCDD (Hogenboom *et al.* 2011). Studies also show that the relative high levels of PCDD/PCDF in human milk samples from Congo and Ivory Coast are due to the use of the clay during pregnancy (see example

10m). PCDD/PCDF in ball/kaolinic clays, in particular from quarries where clays are used for human consumption or as animal feed additive, should thus be included in the inventory.

## PART III ANNEXES AND CASE STUDIES

### Annex 1 Toxicity Equivalency Factors

PCDD, PCDF, and PCB typically occur as mixtures of many congeners in samples, including measurements at the sources (*i.e.*, used in inventory development), in the environment or in biota including humans and wildlife. First risk assessments only focused on the most toxic congener, the 2,3,7,8-Cl<sub>4</sub>DD. Soon it was recognized, though, that all PCDD/PCDF substituted at least in position 2, 3, 7, or 8 are highly toxic and thus, major contributors to the overall toxicity of the “dioxin” mixture.

For regulatory purposes so-called toxicity equivalency factors (TEFs) have been developed for risk assessment of complex mixtures of PCDD/PCDF and later for PCB by different organizations. It should be noted that the first globally applied scheme, the International toxicity equivalency factors (I-TEFs) (NATO/CCMS 1988) did only include the 17 2,3,7,8-substituted PCDD/PCDF congeners. Dioxin-like PCB were added later (WHO-TEFs) (van den Berg *et al.* 1998). The most commonly used are summarized in Table III.1.1.

**Table III.1.1. Most commonly used TEF schemes**

Congener	I-TEF	WHO <sub>1998</sub> -TEF	WHO <sub>2005</sub> -TEF
Polychlorinated dibenzo- <i>p</i> -dioxins			
2378-Cl <sub>4</sub> DD	1	1	1
12378-Cl <sub>5</sub> DD	0.5	1	1
123478-Cl <sub>6</sub> DD	0.1	0.1	0.1
123678-Cl <sub>6</sub> DD	0.1	0.1	0.1
123789-Cl <sub>6</sub> DD	0.1	0.1	0.1
1234678-Cl <sub>7</sub> DD	0.01	0.01	0.01
Cl <sub>8</sub> DD	0.001	0.0001	0.0003
Polychlorinated dibenzofurans			
2378-Cl <sub>4</sub> DF	0.1	0.1	0.1
12378-Cl <sub>5</sub> DF	0.05	0.05	0.03
23478-Cl <sub>5</sub> DF	0.5	0.5	0.3
123478-Cl <sub>6</sub> DF	0.1	0.1	0.1
123678-Cl <sub>6</sub> DF	0.1	0.1	0.1
123789-Cl <sub>6</sub> DF	0.1	0.1	0.1
234678-Cl <sub>6</sub> DF	0.1	0.1	0.1
1234678-Cl <sub>7</sub> DF	0.01	0.01	0.01
1234789-Cl <sub>7</sub> DF	0.01	0.01	0.01
Cl <sub>8</sub> DF	0.001	0.0001	0.0003
Non- <i>ortho</i> polychlorinated biphenyls			
PCB 77	-	0.0001	0.0001
PCB 81	-	0.0001	0.0003
PCB 126	-	0.1	0.1
PCB 169	-	0.01	0.03
Mono- <i>ortho</i> polychlorinated biphenyls			
PCB 105	-	0.0001	0.00003

PCB 114	-	0.0005	0.00003
PCB 118	-	0.0001	0.00003
PCB 123	-	0.0001	0.00003
PCB 156	-	0.0005	0.00003
PCB 157	-	0.0005	0.00003
PCB 167	-	0.00001	0.00003
PCB 189	-	0.0001	0.00003

The toxic equivalent (TEQ) is operationally defined by the sum of the products of the concentration of each congener multiplied by its TEF value. The TEQ is an estimate of the total 2,3,7,8-Cl<sub>4</sub>DD (or TCDD)-like activity of the mixture. Although the scientific basis cannot be considered as solid, the TEF approach has been adopted as an administrative tool by many agencies and allows converting quantitative analytical data for individual PCDD/PCDF congeners into a single toxic equivalent (TEQ). As TEFs are interim values and administrative tools, they are based on present state of knowledge and should be revised, as new data becomes available.

Concurrent with the development of the TEF and TEQ approach for intake situations (humans, fish, birds) has been its application to environmental matrices such as soil, sediment, industrial wastes, soot, fly ash from municipal incinerators, waste water effluents, etc. As such, the TEF approach has been and continues to be used to give a single value to complex environmental matrices.

The Stockholm Convention, according to Annex C, refers to usage of the 1998 TEF scheme that was developed by an expert group under the World Health Organization (WHO) (van den Berg *et al.* 2006).



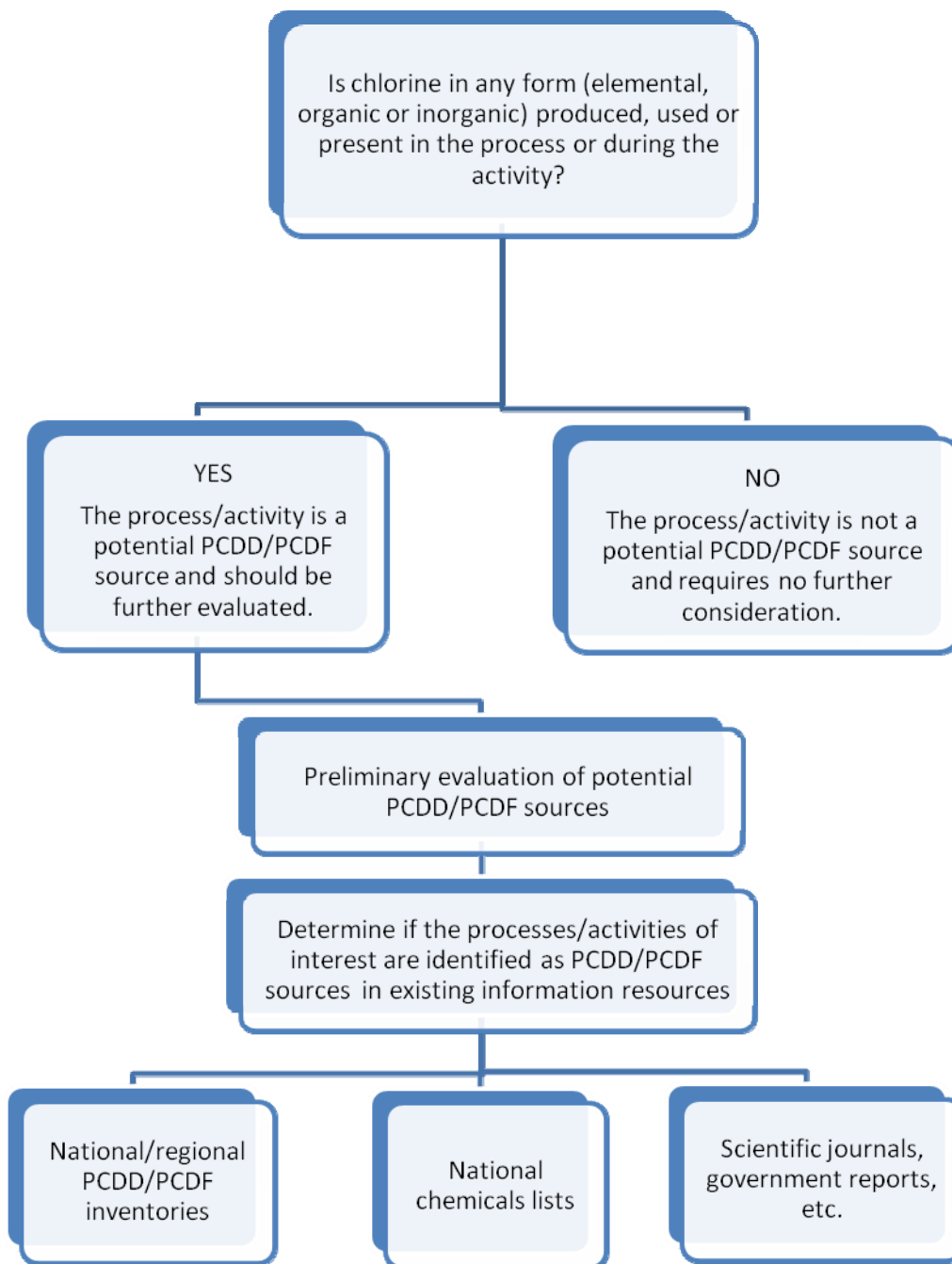
## Annex 2 Guidance on Identifying Sources of PCDD/PCDF

More than 80 PCDD/PCDF sources, each with one or more emission factors, are currently listed in the Toolkit. However, new, yet unlisted sources continue to be identified. These sources attest to the variety of materials and conditions that are associated with PCDD/PCDF formation and release. A brief description of the factors that influence PCDD/PCDF formation and release during industrial chemical production and in combustion processes is given in Chapter 1.4 and further addressed in the BAT/BEP Guidelines.

While carbon, hydrogen and oxygen are common to most industrial chemical production processes as well as processes and activities involving combustion, the possibility of PCDD/PCDF formation exists only when chlorine is also present in elemental, organic or inorganic form. This distinguishing characteristic has been used in identifying some of the PCDD/PCDF sources now listed in the Toolkit. For example, Denmark began the process of identifying PCDD/PCDF sources within its chemical manufacturing sector by selecting and then further evaluating processes that involved any form of chlorine (Hansen 2000). In Germany, a similar strategy was followed in identifying PCDD/PCDF sources among industries in North Rhine-Westphalia (Broker *et al.* 1999) and among thermal processes in the European Union (Wenborn *et al.* 1999). This same strategy can be used to identify new, as-yet unlisted sources as well as hotspots.

PCDD/PCDF source identification can be further refined by the preliminary evaluation shown below, which entails drawing on information in national and regional inventories, national chemical lists, the scientific literature and reports by governments and non-governmental organizations. More in-depth evaluation may also entail assessing the availability of other materials, such as metal catalysts, and conditions, such as temperatures, that are conducive to PCDD/PCDF formation (see, for example, Chapter 1.4, and the BAT/BEP Guidelines, Section VI.F Specific Chemical Production Processes Releasing Chemicals Listed in Annex C) and monitoring gaseous emissions, aqueous discharges, solid residues and products of suspected PCDD/PCDF sources.

Listed in tables III.2.1, III.2.2 and III.2.3 below are industrial chemicals, pesticides and processes or activities that are examples of the potential new sources being reported in the scientific literature, government reports, etc. In their use and/or production some of these may make substantial contributions to national and regional PCDD/PCDF releases. For example, a recent study found PCDD/PCDF as contaminants in 23 pesticides currently used in Australia and estimated that applications of only one of the pesticides, pentachloronitrobenzene (PCNB), may be Australia's largest single PCDD/PCDF source (Holt *et al.* 2010). In addition, preliminary results suggest that post-application photodegradation of PCNB may increase PCDD/PCDF releases by 3 to 4 times (Holt *et al.* 2009). Production of each of the pesticides in this study is a potential PCDD/PCDF source and, as such, deserves careful attention. It is also useful to note that many other chemicals and pesticides were identified in the past as known, suspected or highly probable PCDD/PCDF sources and some of these are still in production today (see Bejarano 2004).



**Figure III.2.1 Simple screening matrix for identifying PCDD/PCDF sources**

**Inventories:** Searches of existing inventories will determine whether other Parties have identified the processes/activities of interest as PCDD/PCDF sources

**National Chemicals Lists:** Some countries have established lists of chemicals that must be tested for PCDD/PCDF before being placed on the market. Such lists include many chemicals that were or are suspected of containing PCDD/PCDF concentrations above certain limits. The processes for producing these chemicals are potential PCDD/PCDF sources.

**Scientific Literature, Government Reports, etc.:** Scientific journals, government reports, and related resources can be searched to determine whether:

1. the processes/activities of interest have been identified as PCDD/PCDF sources;
2. the products, air emissions, wastewater effluents, or other residues of the processes/activities of interest have been found to contain PCDD/PCDF; or
3. the products, air emissions, wastewater effluents or other residues of the processes/activities of interest have been identified as contributing to PCDD/PCDF at “hot spots” – contaminated production sites landfills, dumps, marine and freshwater sediments, soils, etc.
4. the products, air emissions, wastewater effluents or other residues of the processes/activities of interest have been identified as contributing to PCDD/PCDF in surrounding air, soil, vegetation, and/or water; among workers or nearby residents; or among domestic and wild animals, fish, etc.

Included in the following tables are some of the commercial chemicals, pesticides and processes/activities for which studies have found PCDD/PCDF in the products themselves and/or in associated wastes. The presence of PCDD/PCDF in these chemicals and pesticides is evidence of the need for more thorough assessments of the concentrations and frequency of occurrence of PCDD/PCDF in these substances, their production processes and associated emissions, discharges and residues as well as careful evaluation of their management and fate. Similarly, the presence of PCDD/PCDF in one or more wastes attests to the need to assay the PCDD/PCDF content of associated products and to evaluate carefully the management and fate of other process wastes as well as the use of the products.

**Table III.2.1 Commercial chemicals associated with PCDD/PCDF formation and release**

Substance	Associated PCDD/PCDF Release
Hydrogen chloride (HCl, 7647-01-0) and Hydrochloric acid	A survey of chlorinated chemicals production in the Netherlands found PCDD/PCDF at 0.3 pg I-TEQ/L in HCl (van Hattum <i>et al.</i> 2004). In the U.S., PCDD/PCDF concentrations of 20.8 and 28.1 pg I-TEQ/L were measured in samples of sales-grade aqueous hydrochloric acid that was a secondary product of two EDC/VCM/PVC facilities (Vinyl Institute 2002). HCl was also recently identified as the source of PCDD/PCDF contamination in hydrochloric acid used in gelatin production in Europe (Hoogenboom <i>et al.</i> 2007). Most HCl is produced as a secondary product of about 40 manufacturing processes, so emission factors are necessarily specific to those processes.
Sodium hypochlorite (NaOCl, CAS 7681-52-9)	PCDD/PCDF were measured at 4.9 pg TEQ/g in sodium hypochlorite in the only such analysis that was found in the available scientific literature (Rappe 1990). However, contaminated sodium hypochlorite was identified as the source of PCDD/PCDF in sludge from the Swedish textile industry (Lexen 1993).
Metal chlorides	PCDD/PCDF were detected in aluminum chloride (AlCl <sub>3</sub> ), cuprous chloride (CuCl <sub>2</sub> ), cupric chloride (CuCl <sub>3</sub> ), and ferric chloride (FeCl <sub>3</sub> ) in 1986 (Heindl 1986). More recently, high concentrations of PCBs, which are common co-contaminants with PCDD/PCDF, as well as polychloro-bromobiphenyls (PXBs), were reported in FeCl <sub>3</sub> (Nakano 2007).
Acetylene (CAS 74-86-2)	PCDD/PCDF have been reported in wastewater and wastewater treatment sludge from acetylene production by the carbide process. Lee <i>et al.</i> (2009)

	<p>derived an <math>EF_{\text{WATER}}</math> of 5.667 ng TEQ/t for this process, and Jin <i>et al.</i> (2009) derived an <math>EF_{\text{RESIDUE}}</math> of 126.69 <math>\mu\text{g TEQ/t}</math>. PCDD/PCDF were measured at 17,000 pg-TEQ/L in wastewater from the purification of acetylene using sodium hypochlorite (Kawamoto 2002). PCDD/PCDF formation has been attributed to the presence of chlorine-containing impurities in the lime (CaO) that is heated with coke to produce calcium carbide (Jin <i>et al.</i> 2009) and to the use of a chlorine-based oxidizing agent for purifying the crude acetylene (Kawamoto 2002).</p>
Trichloroethylene (CAS 79-01-6)	<p>PCDD/PCDF were reported at a concentration of 0.7 ng TEQ/kg in trichloroethylene made by Solvay in France (van Hattam <i>et al.</i> 2004). PCDD/PCDF have also been found in process residues from trichloroethylene production (Dyke 1997, Wenborn 1999) and in wastewater (Weiss 2006). Trichloroethylene is primarily produced as a secondary product in the production of ethylene dichloride (EDC) by direct chlorination and/or oxychlorination of ethylene.</p>
Epichlorohydrin (1-Chloro-2,3-epoxypropane, CAS 106-89-8)	<p>Production of epichlorohydrin is known to generate large amounts of chlorinated by-products, some of which are released in wastewater and, most probably, in wastewater treatment sludge (Bijsterbosch <i>et al.</i> 1994). PCDD/PCDF have been reported in epichlorohydrin itself and in process wastewater from its production (Fiedler 1994, Lee <i>et al.</i> 2009). Lee <i>et al.</i> (2009) measured PCDD/PCDF in wastewater from an epichlorohydrin production facility in Taiwan and derived an <math>EF_{\text{WATER}}</math> of 5.8 ng TEQ/t. Also a PCDD/PCDF concentration of 1.82 ng TEQ/kg in epichlorohydrin was reported by Fiedler (1994).</p>
Chloroprene(2-chloro-1,3-butadiene, CAS 126-99-8) and Polychloroprene (Neoprene, CAS 9010-98-4) (Polymer of 2-chloro-1,3-butadiene)	<p>PCDD/PCDF were detected at a concentration of 90 ng TEQ/kg in polychloroprene (Neoprene) produced by a Dutch manufacturer (van Hattum <i>et al.</i> 2004). PCDD/PCDF also occurred at 209 pg TEQ/m<sup>3</sup> in vent gases from the same facility, which produced epichlorohydrin, allyl chloride and PVC.</p>
Hexachlorocyclohexane (CAS 608-73-1)	<p>PCDD/PCDF were reported in hexachlorocyclohexane (Zheng <i>et al.</i> 2008).</p>
Tetrachlorobenzene (CAS 95-94-3)	<p>Production of 1,700 tons of tetrachlorobenzene was associated with release in the product of 17.9 g TEQ/year, which suggests an average PCDD/PCDF content in the tetrachlorobenzene of 10,529 ng TEQ/kg (The People's Republic of China 2007).</p>
Chlorinated PVC (C-PVC, CAS 9002-86-2)	<p>PCDD/PCDF as high as 32,000 ng TEQ/kg have been detected in C-PVC (van der Weiden and van der Kolk 2000).</p>
Aromatic polyamides (Aramids) and precursors	<p>PCDD/PCDF were reported at a concentration of 0.137 ng I-TEQ/m<sup>3</sup> in process vent gas (van Hattum <i>et al.</i> 2004) and have also been detected in wastewater (van der Weiden and van der Kolk 2000).</p>
Chlorinated methanes (methylene chloride, chloroform and carbon	<p>Data submitted to the U.S. Environmental Protection Agency show detectable levels of PCDD/PCDF are released in wastewater (Weiss 2006).</p>

tetrachloride)	
Vinylidene chloride (1,1-dichloroethylene CAS 75-35-4)	
Polypropylene	U.S. Toxics Inventory shows reportable quantities of PCDD/PCDF are released in wastewater (USEPA 2004).
Cellulose acetate	
Aliphatic isocyanate resins production	
Polyurethane production	
Meta diisopropenybenzene production	
Adhesion polymers production	
Formaldehyde resins production	
Crosslinking monomers	
Aerosol surfactants	
Coating chemicals	
Fluorochemicals	
Elastomers	
Hytrel polyester elastomer	
Copper chromated arsenate	
Alcohols	
Alumina	
Ethylene	
Paraffins	
Ethoxylates	
PVC-copolymers	PCDD/PCDF were released in vent gases (van der Weiden and van der Kolk 2000).
Sodium dichloroisocyanurate (Sodium troclosene, NADCC, CAS 2893-78-9)	PCDD/PCDF were detected at a concentration of 0.6 pg TEQ/g in detergents containing sodium dichloroisocyanurate (USEPA 2000).
Chlorobenzenes	These chemicals are produced by processes where dioxin-like compounds formation is known to occur (Seys 1997).
Chlorotoluenes	
Chloronitrobenzenes	

**Table III.2.2 Currently-used pesticides recently associated with PCDD/PCDF formation and release**

Pesticide	µg TEQ/t active ingredient, except where noted	Reference
Dichlorprop (2 <i>RS</i> )-2-(2,4-dichlorophenoxy)propionic acid (CAS 120-36-5)	35,000	Hansen (2000)
Nitrophen (NIP) = 2,4-dichlorophenyl-4'-nitrophenyl ether (CAS 1836-75-5)	1,500	Masunaga (1999)
Lindane (γ-hexachlorocyclohexane, γ-HCH) 1α,2α,3β,4α,5α,6β-hexachlorocyclohexane (CAS 58-89-9)	216 <sup>a</sup> (2.1-430 range)	Holt et al. (2010)
Chlorothalonil 2,4,5,6-tetrachloroisophthalonitrile (CAS 1897-45-6)	110 <sup>b</sup>	Holt et al. (2010)
	240	Masunaga (1999)
Dicofol 2,2,2-trichloro-1,1-bis(4-chlorophenyl)ethanol (CAS 115-32-2)	84	Li et al. (2009)
Chlorthal tetrachloroterephthalic acid (CAS 2136-79-0)	58.5 <sup>a</sup> (57-60 range)	Holt et al. (2010)
MCPA/Dicamba 2-Methyl-4-chlorophenoxyacetic acid (CAS 94-74-6) 3,6-Dichloro-2-methoxybenzoic acid (CAS1918-00-9)	48.3 <sup>a</sup> (0.69-96 range)	Holt et al. (2010)
Tiller <ul style="list-style-type: none"> <li>• CPA-2EH ester, 32.1% (<i>RS</i>)-2-ethylhexyl 4-chloro-<i>o</i>-tolylxyacetate (CAS 29450-45-1)</li> <li>• 2,4-D isooctylester, 10.4% iso-octyl (2,4-dichlorophenoxy)acetate (CAS 25168-26-7)</li> <li>• Fenoxaprop-p-ethyl, 4.4% ethyl (<i>R</i>)-2-[4-(6-chloro-1,3-benzoxazol-2-ylloxy)phenoxy]propionate (CAS 71283-80-2)</li> </ul>	19.8 <sup>c</sup>	Huwe et al. (2003)

Fluroxypyr 4-Amino-3,5-dichloro-6-fluoro-2-pyridyloxyacetic acid (CAS 69377-81-7)	17 <sup>b</sup>	Holt et al. (2010)
2,4-DB 4-(2,4-dichlorophenoxy)butyric acid (CAS 94-82-6)	8.8 <sup>a</sup> (7.5-10 range)	Holt et al. (2010)
Assure II = Quizalofop P-Ethyl ethyl (2 <i>R</i> )-2-[4-(6-chloroquinoxalin-2-yl)oxy]phenoxy]propionate (CAS 100646-51-3)	4.1	Huwe et al. (2003)
Imazamox 2-[( <i>RS</i> )-4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl]-5-methoxymethylnicotinic acid (CAS 114311-32-9)	3.1 <sup>a</sup> (1.3-4.9 range)	Holt et al. (2010)
Flumetsulam 2',6'-difluoro-5-methyl[1,2,4]triazolo[1,5- <i>a</i> ]pyrimidine-2-sulfonanilide (CAS 98967-40-9)	2.9 <sup>a</sup> (2.4-3.4 range)	Holt et al. (2010)
MCPA 2-methyl-4-chlorophenoxyacetic acid (CAS 94-74-6)	2.8 <sup>b</sup>	Holt et al. (2010)
	2,000	Masunaga (1999)
Triclopyr/picloram 3,5,6-Trichloro-2-pyridinyloxyacetic acid (CAS 55335-06-3) 4-Amino-3,5,6-trichloro-2-pyridinecarboxylic acid (CAS 1918-02-1)	2.5 <sup>b</sup>	Holt et al. (2010)
Mecoprop/Dicamba = ( <i>RS</i> )-2-(4-chloro-2-methylphenoxy)propanoic acid (CAS 93-65-2 and CAS 7085-19-0) 3,6-Dichloro-2-methoxybenzoic acid (CAS 1918-00-9)	0.068 <sup>b</sup>	Holt et al. (2010)
Fenamiphos ( <i>RS</i> )-(ethyl 4-methylthio- <i>m</i> -tolyl isopropylphosphoramidate) (CAS 22224-92-6)	0.058 <sup>b</sup>	Holt et al. (2010)

<sup>a</sup>Mean of two lower bound values.

<sup>b</sup>Lower bound values

<sup>c</sup>ng TEQ/g of ready-for-use product (active ingredient plus adjuvants).

<sup>d</sup>Mean of four lower bound values.

**Table III.2.3 Additional processes and activities associated with PCDD/PCDF formation and release**

Process/Activity	PCDD/PCDF Release
Precious metals recovery from wastes of jewelry factories and workshops	Incineration with ash recovery is said to be the only viable alternative for recovering precious metals from wastes from jewelry factories and workshops. PCDD/PCDF concentrations in air emissions of various combustion systems were as follows: 0.28 ng TEQ/m <sup>3</sup> for a rotary furnace, afterburner and sleeve filters; 0.41 ng TEQ/m <sup>3</sup> for a

	<p>static furnace, afterburner and sleeve filters; 21 ng TEQ/m<sup>3</sup> for a static furnace, afterburner without carbon system; 0.55 ng TEQ/m<sup>3</sup> for combustion chamber, afterburner and sleeve filters; 0.026 ng TEQ/m<sup>3</sup> combustion chamber, afterburner, sleeve filters, and lime + carbon abatement process (Baldassini <i>et al.</i> 2009).</p>
Heat treatment of food salt	<p>PCDD/PCDF have been detected at considerably higher levels in processed food salt than in natural salt. Comparing bamboo-salt and parched salt, Yang <i>et al.</i> (2004) found PCDD/PCDF levels were generally very low, with bamboo-salt having highest levels – from 5.7 x 10<sup>-5</sup>–0.64 pg TEQ/g. However, another study found considerably higher levels, with baked salts having a range of 1.33 - 16.92 pg TEQ/g and bamboo-salt, a range of 0.71- 23.5 pg TEQ/g (Kim <i>et al.</i> 2002).</p>



## **Annex 3 Questionnaires**

This annex presents sample questionnaires, which can be used to collect information necessary to compile national inventories.

It is particularly practical and appropriate to use individual plant questionnaires to gather information on large point sources<sup>19</sup>. This includes information needed for classification of plants, selection of the appropriate emission factors, and the associated activity rates to calculate emissions.

Since the return rate of the questionnaires is likely to be low, incomplete information-data gaps- will need to be covered by making assumptions about certain source groups, where no specific information can be collected. Approaches will vary, but all assumptions should be clearly described in order to facilitate inventory updates in the following years or revisions in light of improved information.

To determine complete activity rates, a combination of questionnaires (for large point sources) and national statistics should be used.

Sample questionnaires are provided also to facilitate data gathering for entire source groups such as transport or open burning. These questionnaires may be used to assist in the data collection process, but they will most likely need to be complemented by additional information sources. Questionnaires should be accompanied by a cover letter explaining the purpose and context of data gathering, as well as the contact information, reference year, and return date for the questionnaire.

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<sup>19</sup> Large point sources include major industrial emitters, and the collection of information on their activity rates should be given priority. Definition of the large point sources as described for different industrial sectors in Annex 1 of the Directive 2008/1/EC on Integrated Pollution Prevention and Control (IPPC) may be used for orientation. As an example, emission from the following large point sources are regulated by the IPPC directive:

- combustion installations with a rated thermal input exceeding 50 MW;
- installations for the production of iron or steel with a capacity exceeding 2,5 tons per hour;
- installations for the production of cement with a capacity exceeding 500 tons per day, etc.

More details can be found at <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32008L0001:EN:NOT>

Sample cover letter for questionnaire

<b>National Inventory of Unintentional Releases of Persistent Organic Pollutants under the Stockholm Convention</b> <b>Reference Year 20____ (January 1-December 31)</b>	
<b>Requested by:</b>	[Institution's name with street address; contact person with phone and fax number; e-mail address]
<b>To:</b>	[Institution's name with street address and other coordinates]
<b>Purpose and context:</b>	[Name of the country] adopted the Stockholm Convention on [date of adoption]. One of the obligations of [name of the country] under the Convention is the reduction of releases of unintentionally produced persistent organic pollutants. To achieve this goal, [name of the country] needs to identify, characterize, quantify and prioritize sources of releases of these chemicals. As part of the data collection process for the national inventory, this questionnaire is used to retrieve the information needed for classification of facilities, selection of emission factors, and estimation of activity rates to allow calculation of releases. Inventory results will be used in the development of national strategies to minimize releases, as requested by the Convention.
<b>Please return the completed questionnaire to</b> _____ <b>(Date)</b> <b>the above sender not later than</b>	

**Questionnaire 1: Group 1 - Waste Incineration**

Type of Plant	Municipal solid waste	[ ]
	Industrial waste	[ ]
	Hospital waste	[ ]
	Light shredder	[ ]
	Sewage sludge	[ ]
	Waste wood and waste biomass	[ ]
	Animal carcasses	[ ]
Name of Plant		
Location (City/Province)		
Address		
Contact (Name, position, phone and fax numbers, e-mail)		
Number of Furnaces		
Type of Operation	Batch ( <i>e.g.</i> , 100 kg per batch)	[ ]
	Semi-continuous ( <i>e.g.</i> , 8 hours per day)	[ ]
	Continuous (24 hours per day)	[ ]
Annual Operational/Capacity (per Unit)	t/h (tons per hour)	
	h/d (hours per day)	
	d/w (days per week)	
	t/d (tons per day)	
	d/a (days per year)	
	h/a (hours per year)	
	t/a (tons per year)	
Annual Operation/Capacity (total)	t/h (tons per hour)	
	h/d (hours per day)	
	d/w (days per week)	
	t/d (tons per day)	
	d/a (days per year)	
	h/a (hours per year)	
	t/a (tons per year)	
Type of Furnace	Mass burn waterwall (grate)	
	Fluidized bed	
	Stoker	
	Rotary kiln	
	Other (please specify)	
Temperature in Furnace	Main furnace (°C)	
	Afterburner/second chamber (°C)	
Type of Air Pollution Control System (APCS)	Electrostatic precipitator	[ ]
	Cyclone	[ ]

	Bag filter	[ ]
	Wet scrubber	[ ]
	Dry scrubber	[ ]
	Lime injection	[ ]
	NaOH/alkali injection	[ ]
	Active carbon/coke injection	[ ]
	Active carbon filter	[ ]
	Catalytic converter (SCR)	[ ]
	Induced or forced draft fan	[ ]
	Other (please specify)	
	None	[ ]
Heat Recovery System	Yes [ ]	No [ ]
Temperature of Gases	At entry to APCS (°C) [ ]	At exit from APCS (°C) [ ]
Flux of Exit Gases	(m <sup>3</sup> /h) (dry gas)	

Residues		Disposal of these Residues	
Generation of Bottom Ashes	t/a [ ]	Recirculation [ ]	Landfill [ ]
Generation of Fly Ashes	t/a [ ]	Recirculation [ ]	Landfill [ ]
Generation of (Waste)Water	t/a [ ]	Disposal	
Generation of Sludges (as dry matter)	t/a [ ]	Recirculation [ ]	Landfill [ ]

**Final classification and evaluation** (to be filled out by the data evaluator)

Class	Emission Factor (µg TEQ/t)				
	Air	Water	Land	Product	Residues
Annual Activity (t/a)	Annual Release (g TEQ/a)				
	Air	Water	Land	Product	Residues

**Questionnaire 2: Group 2 – Ferrous and Non-Ferrous Metal Production**

Type of Plant	Sinter	[ ]	
	Coke	[ ]	
	Iron and/or steel	Primary [ ]	Secondary [ ]
	Foundry	Primary [ ]	Secondary [ ]
	Copper	Primary [ ]	Secondary [ ]
	Aluminum	Primary [ ]	Secondary [ ]
	Lead	Primary [ ]	Secondary [ ]
	Zinc	[ ]	
	Brass/Bronze	Primary [ ]	Secondary [ ]
	Magnesium	[ ]	
	Other non-ferrous metal	Primary [ ]	Secondary [ ]
	Shredder	[ ]	
	Other	Primary [ ]	Secondary [ ]
Address			
Contact (Name, position, phone and fax numbers, e-mail)			
Number of Furnaces			
Type of Operation	Batch (e.g., 100 kg per batch)	[ ]	
	Semi-continuous (e.g., 8 hours per day)	[ ]	
	Continuous (24 hours per day)	[ ]	
Annual Operational/Capacity (per Unit)	t/h (tons per hour)		
	h/d (hours per day)		
	d/w (days per week)		
	t/d (tons per day)		
	d/a (days per year)		
	h/a (hours per year)		
	t/a (tons per year)		
Annual Operation/Capacity (total)	t/h (tons per hour)		
	h/d (hours per day)		
	d/w (days per week)		
	t/d (tons per day)		
	d/a (days per year)		
	h/a (hours per year)		
	t/a (tons per year)		
Type of Furnace	Blast furnace		
	Induction furnace		
	Electric arc furnace (EAF)		
	Cowper		
	Rotary kiln		
	Reverberatory		

	Other (please specify)	
Temperature in Furnace	Main furnace (°C) Second chamber/afterburner (°C)	
Primary Fuel	Type	t/a
Secondary/Alternative Fuel	Type	t/a or%
Type of Air Pollution Control System (APCS)	Electrostatic precipitator	[ ]
	Cyclone	[ ]
	Bagfilter	[ ]
	Wet scrubber	[ ]
	Dry scrubber	[ ]
	Lime injection	[ ]
	NaOH/alkali injection	[ ]
	Active carbon/coke injection	[ ]
	Active carbon filter	[ ]
	Catalytic converter (SCR)	[ ]
	Induced or forced draft fan	[ ]
Other (please specify)		
None	[ ]	
Heat Recovery System	Yes [ ]	No [ ]
Temperature of Gases	At entry to APCS (°C) [ ]	At exit from APCS (°C) [ ]
Flux of Exit Gases	(m <sup>3</sup> /h) (dry gas)	

Residues		Disposal of these Residues	
Generation of Bottom Ashes	t/a [ ]	Recirculation [ ]	Landfill [ ]
Generation of Fly Ashes	t/a [ ]	Recirculation [ ]	Landfill [ ]
Generation of (Waste)Water	t/a [ ]	Disposal	
Generation of Sludges (as dry matter)	t/a [ ]	Recirculation [ ]	Landfill [ ]

**Final classification and evaluation** (to be filled out by the data evaluator)

	<b>Emission Factor (µg TEQ/t)</b>				
<b>Class</b>	<b>Air</b>	<b>Water</b>	<b>Land</b>	<b>Product</b>	<b>Residues</b>
	<b>Annual Release (g TEQ/a)</b>				
<b>Annual Activity (t/a)</b>	<b>Air</b>	<b>Water</b>	<b>Land</b>	<b>Product</b>	<b>Residues</b>

**Questionnaire 3: Group 3 – Power Generation and Heating**

Type of Plant	<b>Power plants</b>	
	Coal	[ ]
	Lignite	[ ]
	Bituminous coal	[ ]
	Anthracite	[ ]
	Other	[ ]
	Natural gas	[ ]
	Wood	[ ]
	Landfill gas	[ ]
	Sewer gas	[ ]
	Biomass (please specify)	
	<b>Industrial Combustion units (small)</b>	
	Coal (please specify)	[ ]
	Lignite	[ ]
	Bituminous coal	
Anthracite	[ ]	
Other	[ ]	
Natural wood	[ ]	
Combustion of other kinds of biomass		
Sugar cane	[ ]	
Tapioka	[ ]	
Cotton	[ ]	
Bamboo	[ ]	
Banana	[ ]	
Harvest residues	[ ]	
Other (please specify)	[ ]	
Other (please specify)		
Address		
Contact (Name, position, phone and fax numbers, e-mail)		
Type of Operation	Batch (e.g., 100 kg per batch)	[ ]
	Semi-continuous (e.g., 8 hours per day)	[ ]
	Continuous (24 hours per day)	[ ]
Annual Operation/Capacity (per Unit)	t/h (tons per hour) or TJ/h (Terajoule per hour)	
	h/d (hours per day)	
	d/w (days per week)	
	t/d (tons per day) or TJ/h (Terajoule per day)	
	d/a (days per year)	
	h/a (hours per year)	
	t/a (tons per year) or TJ/h (Terajoule per year)	
Annual Operation/Capacity	d/a (days per year)	

(total)	h/a (hours per year) TJ/a (Terajoule per year)	
Type of Furnace/Combustor	Boiler Process heater Flare Turbine (internal gas) Combustion engine (internal) Other (please specify)	
Temperature in Furnace	Main furnace (°C) Second chamber/afterburner (°C)	
Type of Abatement Pollution Control System (APCS)	Electrostatic precipitator Cyclone Bughouse filter Wet scrubber Dry scrubber Lime injection NaOH/alkali injection Active carbon/coke injection Active carbon filter Catalytic converter (SCR) Other (please specify) None	[ ] [ ] [ ] [ ] [ ] [ ] [ ] [ ] [ ] [ ] [ ]
Heat Recovery System	Yes [ ]	No [ ]
Temperature of Gases	At entry to APCS (°C) [ ]	At exit from APCS (°C) [ ]
Flux of Exit Gases	(m <sup>3</sup> /h) (dry gas)	

Residues		Disposal of these Residues	
Generation of Bottom Ashes	t/a [ ]	Recirculation [ ]	Landfill [ ]
Generation of Fly Ashes	t/a [ ]	Recirculation [ ]	Landfill [ ]
Generation of (Waste)Water	t/a [ ]	Disposal	
Generation of Sludges (as dry matter)	t/a [ ]	Recirculation [ ]	Landfill [ ]

**Final classification and evaluation** (to be filled out by the data evaluator)

Class	Emission Factor (µg TEQ/t)				
	Air	Water	Land	Product	Residues
Annual Activity (t/a)	Annual Release (g TEQ/a)				
	Air	Water	Land	Product	Residues



**Questionnaire 4: Group 4 – Mineral Production**

Type of Plant	Cement	[ ]
	Lime	[ ]
	Brick	[ ]
	Glass	[ ]
	Ceramics	[ ]
	Asphalt mixing	[ ]
Address		
Contact (Name, position, phone and fax numbers, e-mail)		
Number of Furnaces		
Feed Materials (type, quantity = t/a)		
Primary Fuel (type, quantity = t/a)		
Secondary/Alternative Fuel (type, quantity = t/a)		
Type of Process	Dry [ ]	Wet [ ]
Type of Operation	Batch (e.g., 100 kg per batch)	[ ]
	Semi-continuous (e.g., 8 hours per day)	[ ]
	Continuous (24 hours per day)	[ ]
Annual Operational/Capacity (per Unit)	t/h (tons per hour)	
	h/d (hours per day)	
	d/w (days per week)	
	t/d (tons per day)	
	d/a (days per year)	
	h/a (hours per year)	
Annual Operation/Capacity (total)	t/h (tons per hour)	
	h/d (hours per day)	
	d/w (days per week)	
	t/d (tons per day)	
	d/a (days per year)	
	h/a (hours per year)	
Type of Furnace	Rotary kiln	
	Shaft kiln	
	Tunnel furnace	

	Other (please specify)	
Temperature in Furnace	Main furnace (°C)	
	Second chamber/afterburner (°C)	
Type of Air Pollution Control System (APCS)	Electrostatic precipitator	[ ]
	Cyclone	[ ]
	Bagfilter	[ ]
	Wet scrubber	[ ]
	Dry scrubber	[ ]
	Lime injection	[ ]
	NaOH/alkali injection	[ ]
	Active carbon/coke injection	[ ]
	Active carbon filter	[ ]
	Catalytic converter (SCR)	[ ]
	Induced or forced draft fan	[ ]
	Other (please specify)	[ ]
None	[ ]	
Heat Recovery System	Yes [ ]	No [ ]
Temperature of Gases	At entry to APCS (°C) [ ]	At exit from APCS (°C) [ ]
Flux of Exit Gases	(m <sup>3</sup> /h) (dry gas)	

Residues		Disposal of these Residues	
Generation of Bottom Ashes	t/a [ ]	Recirculation [ ]	Landfill [ ]
Generation of Fly Ashes	t/a [ ]	Recirculation [ ]	Landfill [ ]
Generation of (Waste)Water	t/a [ ]	Disposal	
Generation of Sludges (as dry matter)	t/a [ ]	Recirculation [ ]	Landfill [ ]

**Final classification and evaluation** (to be filled out by the data evaluator)

Class	Emission Factor (µg TEQ/t)				
	Air	Water	Land	Product	Residues
Annual Activity (t/a)	Annual Release (g TEQ/a)				
	Air	Water	Land	Product	Residues

**Questionnaire 5: Group 5 – Transport**

Region/Province/Nation.			
Address			
Contact (Name, position, phone and fax numbers, e-mail)			
<b>Type of fuel</b>	<b>Leaded Gasoline</b>	<b>Unleaded Gasoline</b>	<b>Diesel/Light Fuel Oil</b>
Annual national fuel consumption in liter per year (L/a)			
<b>Passenger Cars</b>			
Number of vehicles			
Annual road performance per vehicle and kilometer (km/a)			
Fuel consumption (L/km; L/a)			
Total annual consumption (L/a)			
APCS* (Yes/No)			
<b>Busses</b>			
Number of busses			
Annual road performance per vehicle and year (km/a)			
Fuel consumption (L/km; L/a)			
Total annual consumption (L/a)			
Annual consumption in tons per year (t/a)			
APCS (Yes/No)			
<b>Busses and Trucks</b>			
Number of busses			
Annual road performance per vehicle and year (km/a)			
Fuel consumption (L/km; L/a)			
Total annual consumption (L/a)			
Annual consumption in tons per year (t/a)			
APCS (Yes/No)			
<b>Ships</b>			
Number of ships			
Annual performance per vehicle and year (km/a)			
Fuel consumption (L/km; L/a)			
Total annual consumption (L/a)			

Annual consumption in tons per year (t/a)			
APCS (Yes/No)			
<b>Trains</b>			
Number of trains (on any of the above fuels)			
Annual railroad performance per vehicle and year (km/a)			
Fuel consumption (L/km; L/a)			
Total annual consumption (L/a)			
Annual consumption in tons per year (t/a)			
APCS (Yes/No)			

**Final classification and evaluation** (to be filled out by the data evaluator)

Class	Emission Factor ( $\mu\text{g TEQ/t}$ )				
	Air	Water	Land	Product	Residues
Annual Activity (t/a)	Annual Release (g TEQ/a)				
	Air	Water	Land	Product	Residues

\*APCS: means catalyst for gasoline and particulate removal for Diesel

**Questionnaire 6: Group 6 - Open Burning Processes**

Region/Province/Nation.							
Address							
Contact (Name, position, phone and fax numbers, e-mail)							
<b>Biomass burning</b>							
Type of biomass, <i>e.g.</i> , pine, sugarcane, <i>etc.</i>	Amount of biomass per hectare burned (t/ha)	Area burned per hectare and year (ha/a)		Amount of biomass burned in tons per year (t/a)			
1.							
2.							
3.							
4.							
Total							
<b>Open Waste Burning and Accidental Fires</b>							
General waste statistics							
Tons of waste generated	Per capita and day		Per capita and year		Nationally per year (t)		
Type of source	Amount of waste burned per capita (t/a)		Number of inhabitants		Amount of waste burned per year (t/a)		
	(%)	(t/a)	(%)	(t/a)	(%)	(t/a)	
1. Landfill fires							
2. Open burning of domestic waste							
3. Open burning of wood (construction/demolition)							
Region/Province/Nation-wide	Number of houses burned per year (No/a)			Number of vehicles burned per year (No/a)			
4. Accidental fires in houses, factories							
5. Accidental fires in vehicles							

**Final classification and evaluation** (to be filled out by the data evaluator)

Class	Emission Factor ( $\mu\text{g TEQ/t}$ )				
	Air	Water	Land	Product	Residues
Annual Activity (t/a)	Annual Release (g TEQ/a)				
	Air	Water	Land	Product	Residues

**Questionnaire 7: Group 7 – Production and Use of Chemicals and Consumer Goods (releases into air and into water)**

Chemical Industry: Type of Plant	Pulp and paper industry: Pulp	[ ]
	Pulp and paper industry: Paper (primary or recycling)	[ ]
	Pulp and paper - integrated	[ ]
	Organochlorine production	
	Ethylene dichloride	[ ]
	PVC	[ ]
	Pesticides (PCP, 2,4,5-T, 2,4-D)	[ ]
	Production of chlorine gas (graphite electrodes)	[ ]
Petroleum industry refineries	[ ]	
Address		
Contact (Name, position, phone and fax numbers, e-mail)		
Capacity: Consumption of Raw Materials (type, quantity = t/a)		
Capacity: Final Product of Raw Materials (type, quantity = t/a)		
Type of Process	Fixed-bed	[ ]
	Fluidized bed	[ ]
	Other	[ ]
Type of Operation	Batch (e.g., 100 kg per batch)	[ ]
	Semi-continuous (e.g., 8 hours per day)	[ ]
	Continuous (24 hours per day)	[ ]
Annual Operation/Capacity (per Unit)	t/h (tons per hour)	
	h/d (hours per day)	
	d/w (days per week)	
	t/d (tons per day)	
	d/a (days per year)	
	h/a (hours per year)	
	t/a (tons per year)	
Annual Operation/Capacity (total)	t/h (tons per hour)	
	h/d (hours per day)	
	d/w (days per week)	
	t/d (tons per day)	
	d/a (days per year)	
	h/a (hours per year)	
	t/a (tons per year)	

Operation/Production Temperature	(°C)		
Water discharge (L/h, m <sup>3</sup> /a)			
Water treatment	Settling pond	[ ]	
	Aerated lagoon	[ ]	
	Secondary treatment	[ ]	
	Tertiary Treatment	[ ]	
	Others (please specify)	[ ]	
Sludge generation	t/a (tons per year)		
Sludge disposal	Landfill (t/a)		
	Land farming (t/a)		
	On-site (t/a)		
	Incineration (t/a)		
	Others (please specify) (t/a)		
Type of Air Pollution Control System (APCS)	Electrostatic precipitator	[ ]	
	Cyclone	[ ]	
	Bag filter	[ ]	
	Wet scrubber	[ ]	
	Dry scrubber	[ ]	
	Lime injection	[ ]	
	NaOH/alkali injection	[ ]	
	Active carbon/coke injection	[ ]	
	Active carbon filter	[ ]	
	Catalytic converter (SCR)	[ ]	
	Induced or forced draft fan	[ ]	
	Other (please specify)		
None	[ ]		
Temperature of Gases	At entry to APCS (°C) [ ]	At exit from APCS (°C) [ ]	
Flux of Exit Gases	(m <sup>3</sup> /h) (dry gas)		
Residues		Disposal of these Residues	
Generation of Bottom Ashes	t/a [ ]	Recirculation [ ]	Landfill [ ]
Generation of Fly Ashes	t/a [ ]	Recirculation [ ]	Landfill [ ]
Generation of (Waste)Water	t/a [ ]	Disposal	
Generation of Sludges (as dry matter)	t/a [ ]	Recirculation [ ]	Landfill [ ]

**Final classification and evaluation** (to be filled out by the data evaluator)

Class	Emission Factor (µg TEQ/t)				
	Air	Water	Land	Product	Residues
Annual Activity (t/a)	Annual Release (g TEQ/a)				
	Air	Water	Land	Product	Residues

## Annex 4    **Compilation of all emission factors**

This annex contains a compilation of all emission factors for the ten source categories. These sheets are also available as EXCEL files to be used directly for calculation of the annual releases via all vectors.

In the following tables, the majority of the emission factors are given as  $\mu\text{g TEQ}$  per ton of feed material or product, respectively. In a few exemptions, *e.g.*, residues from coal fired stoves in domestic heating (category 3e) as well as for water releases in group 9, the annual releases are estimated on basis of residues generated. For other estimates, *e.g.*, water and residue releases from the pulp and paper industry, the preferred option may also be to calculate the annual releases based on volume discharged and concentration in the water or residue, respectively.

Care should also be taken that annual releases are not counted twice; *e.g.* the residue from one process may be feed material for another process or activity. Examples are ashes from the ferrous and non-ferrous metal industry, which may be utilized in secondary processes. Further, wastewater from industrial processes normally should be accounted to the respective industry where they are generated. However, occasionally, statistics may provide data at the disposal site, for example the amount of wastewater discharged at a specific location may be known; *e.g.* for open water dumping or discharges at sewer plants. Thus, special care should be taken when numbers are being filled in, especially for group 9.

In the following tables:

“NA” denotes that the vector is not expected.

“ND” denotes that presently there is no suitable emission factor available. This means that this vector can be of importance but presently, releases along this vector cannot be calculated.

“LoC” denotes the level of confidence assigned to a specific emission factor.

“H” denotes a high level of confidence.

“M” denotes a medium level of confidence.

“L” denotes a low level of confidence.



**Table III.4.1 Emission factors for group 1 – Waste Incineration**

Group	Cat.	Class	Source categories	Potential Release Route (µg TEQ/t)					
				Air	Water	Land	Product	Residue	
								Fly Ash	Bottom Ash
<b>1</b>			<b>Waste incineration</b>						
	<b>a</b>		<b>Municipal solid waste incineration</b>						
		1	Low technol. combustion, no APCS <i>LoC M</i>	3,500		NA	NA	ND	75
		2	Controlled comb., minimal APCS <i>LoC M</i>	350		NA	NA	500	15
		3	Controlled comb., good APCS <i>LoC M</i>	30		NA	NA	200	7
		4	High tech. combustion, sophisticated APCS <i>LoC M</i>	0.5		NA	NA	15	1.5
	<b>b</b>		<b>Hazardous waste incineration</b>						
		1	Low technol. combustion, no APCS <i>LoC L</i>	35,000		NA	NA	9,000	
		2	Controlled comb., minimal APCS <i>LoC L</i>	350		NA	NA	900	
		3	Controlled comb., good APCS <i>LoC L</i>	10		NA	NA	450	
		4	High tech. combustion, sophisticated APCS <i>LoC L</i>	0.75		NA	NA	30	
	<b>c</b>		<b>Medical waste incineration</b>						
		1	Uncontrolled batch combustion, no APCS <i>LoC L</i>	40,000		NA	NA		200
		2	Controlled, batch, no or minimal APCS <i>LoC L</i>	3,000		NA	NA		20
		3	Controlled, batch comb., good APCS <i>LoC M</i>	525		NA	NA	920	
		4	High tech, continuous, sophisticated APCS <i>LoC M</i>	1		NA	NA	150	
	<b>d</b>		<b>Light fraction shredder waste incineration</b>						
		1	Uncontrolled batch comb., no APCS <i>LoC L</i>	1,000		NA	NA	ND	
		2	Controlled, batch, no or minimal APCS <i>LoC M</i>	50		NA	NA	ND	
		3	High tech, continuous, sophisticated APCS <i>LoC M</i>	1		NA	NA	150	

<b>e</b>	<b>Sewage sludge incineration</b>						
	1	Old furnaces, batch, no/little APCS <i>LoC</i>	50 <i>M</i>		NA	NA	23 <i>M</i>
	2	Updated, continuously, some APCS <i>LoC</i>	4 <i>M</i>		NA	NA	0.5 <i>M</i>
	3	State-of-the-art, full APCS <i>LoC</i>	0.4 <i>M</i>		NA	NA	0.5 <i>M</i>
<b>f</b>	<b>Waste wood and waste biomass incineration</b>						
	1	Old furnaces, batch, no/little APCS <i>LoC</i>	100 <i>M</i>		NA	NA	1,000 <i>M</i>
	2	Updated, continuously, some APCS <i>LoC</i>	10 <i>M</i>		NA	NA	10 <i>M</i>
	3	State-of-the-art, full APCS <i>LoC</i>	1 <i>M</i>		NA	NA	0.2 <i>M</i>
<b>g</b>	<b>Animal carcasses burning</b>						
	1	Old furnaces, batch, no/little APCS <i>LoC</i>	500 <i>M</i>		NA	NA	ND
	2	Updated, continuously, some APCS <i>LoC</i>	50 <i>M</i>		NA	NA	ND
	3	State-of-the-art, full APCS <i>LoC</i>	5 <i>M</i>		NA	NA	ND

**Table III.4.2 Emission factors for group 2 – Ferrous and Non-ferrous Metal Production**

Group	Cat.	Class	Source categories	Potential Release Route (µg TEQ/t)						
				Air	Water	Land	Product	Residue		
2	a	<b>Ferrous and Non-Ferrous Metal Production</b>								
		1	<b>Iron ore sintering</b> High waste recycling, incl. oil contaminated materials, no or limited air pollution control	20	ND	ND	ND	0.003		
			LoC	M				L		
		2	Low waste use, well controlled plant	5	ND	ND	ND	1		
			LoC	H				L		
		3	High technology, emission reduction	0.3	ND	ND	ND	2		
			LoC	H				M		
		b	<b>Coke production</b>							
			1	No gas cleaning	3	0.06	ND	ND	ND	
		LoC	M	M						
	2	Afterburner/dust removal	0.03	0.06	ND	ND	ND			
		LoC	M	M						
	c	<b>Iron and steel production plants and foundries</b>								
		<b>Iron and steel plants</b>								
		1	Dirty scrap, scrap preheating, limited controls	10	ND	NA	NA	15		
			LoC	H				M		
		2	Clean scrap/virgin iron or dirty scrap, afterburner, fabric filter	3	ND	NA	NA	15		
			LoC	H				H		
		3	Clean scrap/virgin iron or dirty scrap, EAF equipped with APC designed for low PCDD/PCDF emission, BOF furnaces	0.1	ND	NA	NA	0.1		
			LoC	H				M		
	4	Blast furnaces with APCS	0.01	ND	NA	NA	ND			
		LoC	H							
	<b>Foundries</b>									
	1	Cold air cupola or hot air cupola or rotary drum, no APCS	10	ND	NA	NA	ND			
		LoC	M							
	2	Rotary drum - fabric filter or wet scrubber	4.3	ND	NA	NA	0.2			
	LoC	M				L				
3	Cold air cupola, fabric filter or wet scrubber	1	ND	NA	NA	8				
	LoC	M				L				
4	Hot air cupola or induction furnace, fabric filter or wet scrubber	0.03	ND	NA	NA	0.5				
	LoC	M				M				
	<b>Hot-dip galvanizing plants</b>									
	1	Facilities without APCS	0.06	NA	NA	NA	0.01			
	LoC	M				L				
2	Facilities without degreasing step, good APCS	0.05	NA	NA	NA	2				

		LoC	M				L
	3	Facilities with degreasing step, good APCS	0.02	NA	NA	NA	1
		LoC	M				L
<b>d</b>		<b>Copper production</b>					
	1	Sec. Cu - Basic technology	800	0.5	NA	NA	630
		LoC	M	M			L
	2	Sec. Cu - Well controlled	50	0.5	NA	NA	630
		LoC	H	M			L
	3	Sec. Cu - Optimized for PCDD/PCDF control	5	0.5	NA	NA	300
		LoC	M	M			M
	4	Smelting and casting of Cu/Cu alloys	0.03	0.5	NA	NA	ND
		LoC	M	M			
	5	Prim. Cu, well-controlled, with some secondary feed materials	0.01	0.5	NA	NA	ND
		LoC	H	M			
	6	Pure prim. Cu smelters with no secondary feed	ND	0.5	NA	NA	NA
		LoC		M			
<b>e</b>		<b>Aluminum production</b>					
	1	Processing scrap Al, minimal treatment of inputs, simple dust removal	100	ND	NA	NA	200
		LoC	M				M
	2	Scrap treatment, well-controlled, fabric filter, lime injection	3.5	ND	NA	NA	400
		LoC	H				M
	3	Optimized process for PCDD/PPCDF abatement	0.5	ND	NA	NA	100
		LoC	M				M
	4	Shavings/turnings drying (simple plants)	5.0	NA	NA	NA	NA
		LoC	M				
	5	Thermal de-oiling, rotary furnaces, afterburners, fabric filters	0.3	NA	NA	NA	NA
		LoC	M				
	6	Primary Al plants	ND	NA	NA	NA	ND
<b>f</b>		<b>Lead production</b>					
	1	Lead production from scrap containing PVC	80	ND	NA	NA	ND
		LoC	M				
	2	Lead production from PVC/Cl2 free scrap, some APCS	8	ND	NA	NA	50
		LoC	H				H
	3	Lead production from PVC/Cl2 free scrap in highly efficient furnaces, with APC including scrubbers	0.05	ND	NA	NA	ND
		LoC	M				
	4	Pure primary lead production	0.4	ND	NA	NA	ND
		LoC	M				
<b>g</b>		<b>Zinc production</b>					
	1	Kiln with no dust control	1,000	ND	NA	NA	0.02

		LoC	M				M
	2	Hot briquetting/rotary furnaces, basic control	100	ND	NA	NA	1*
		LoC	H				M
	3	Comprehensive control	5	ND	NA	NA	1*
		LoC	H				M
	4	Zinc melting and primary zinc production	0.1	ND	NA	NA	ND
		LoC	M				
<b>h</b>		<b>Brass and bronze production</b>					
	1	Thermal de-oiling of turnings	2.5	NA	NA	NA	NA
		LoC	H				
	2	Simple melting furnaces	10	ND	NA	NA	ND
		LoC	M				
	3	Mixed scarp, induction furnace, bagfilter	3.5	ND	NA	NA	125
		LoC	H				M
	4	Sophisticated equipment, clean inputs, good APCS	0.1	ND	NA	NA	ND
		LoC	H				
<b>i</b>		<b>Magnesium production</b>					
	1	Using MgO/C thermal treatment in Cl <sub>2</sub> , no effluent treatment, poor APCS	250	9,000	NA	NA	0
		LoC	M	M			
	2	Using MgO/C thermal treatment in Cl <sub>2</sub> , comprehensive pollution control	50	30	NA	NA	9,000
		LoC	H	H			M
	3	Thermal reduction process	3	ND	NA	NA	NA
		LoC	H				
<b>j</b>		<b>Thermal Non-ferrous metal production (e.g., Ni)</b>					
	1	Contaminated scrap, simple or no APCS	100	ND	NA	NA	ND
		LoC	M				
	2	Clean scrap, good APCS	2	ND	NA	NA	ND
		LoC	M				
<b>k</b>		<b>Shredders</b>					
	1	Metal shredding plants	0.2	NA	NA	ND	5
		LoC	H				H
<b>l</b>		<b>Thermal wire reclamation and e-waste recycling</b>					
	1	Open burning of cable	12,000	ND	ND	ND	ND
		LoC	M				
	2	Open burning of circuit boards	100	ND	ND	ND	ND
		LoC	M				
	3	Basic furnace with after burner, wet scrubber	40	ND	NA	ND	ND
		LoC	M				
	4	Burning electric motors, brake shoes, etc., afterburner	3.3	ND	NA	ND	ND
		LoC	M				

\* In some cases (e.g. Waelz kilns) emission factors for residues can be as high as 2,000 µg TEQ/t of zinc

**Table III.4.3 Emission factors for group 3 – Power Generation and Heating**

Group	Cat.	Class	Source categories	Potential Release Route (µg TEQ/TJ)				
				Air	Water	Land	Product	Residue
<b>3</b>			<b>Heat and Power Generation</b>					
	<b>a</b>		<b>Fossil fuel power plants</b>					
		1	Fossil fuel/waste co-fired power boilers <i>LoC</i>	35 <i>L</i>	ND	NA	NA	ND
		2	Coal fired power boilers <i>LoC</i>	10 <i>M</i>	ND	NA	NA	14 <i>H</i>
		3	Peat fired power boilers <i>LoC</i>	17.5 <i>L</i>	ND	NA	NA	ND
		4	Heavy fuel fired power boilers <i>LoC</i>	2.5 <i>M</i>	ND	NA	NA	ND
		5	Shale oil fired power plants <i>LoC</i>	1.5 <i>L</i>	ND	NA	NA	ND
		6	Light fuel oil/natural gas fired power boilers <i>LoC</i>	0.5 <i>H</i>	ND	NA	NA	ND
	<b>b</b>		<b>Biomass power plants</b>					
		1	Mixed biomass fired power boilers <i>LoC</i>	500 <i>M</i>	ND	NA	NA	ND
		2	Clean wood fired power boilers <i>LoC</i>	50 <i>H</i>	ND	NA	NA	15 <i>H</i>
		3	Straw fired boilers <i>LoC</i>	50 <i>M</i>	ND	NA	NA	70 <i>M</i>
		4	Boilers fired with bagasse, rice husk etc. <i>LoC</i>	50 <i>L</i>	ND	NA	NA	50 <i>L</i>
	<b>c</b>		<b>Landfill biogas combustion</b>					
		1	Biogas-/landfill gas fired boilers, motors/turbines and flaring <i>LoC</i>	8 <i>M</i>	ND	NA	NA	NA
	<b>d</b>		<b>Household heating and cooking - Biomass</b>					µg TEQ/t Ash
		1	Contaminated biomass fired stoves <i>LoC</i>	1,500 <i>L</i>	ND	ND	NA	1,000 <i>L</i>
		2	Virgin biomass fired stoves (advanced technology) <i>LoC</i>	100 <i>M</i>	ND	ND	NA	10 <i>M</i>
		3	Straw fired stoves <i>LoC</i>	450 <i>L</i>	ND	ND	NA	30 <i>L</i>
		4	Charcoal fired stoves <i>LoC</i>	100 <i>L</i>	ND	ND	NA	0.1 <i>L</i>
		5	Open-fire (3-stone) stoves (virgin wood) <i>LoC</i>	20 <i>L</i>	ND	ND	NA	0.1 <i>L</i>

		6	Simple stoves (virgin wood) <i>LoC</i>	100 <i>L</i>	ND	ND	NA	0.1 <i>L</i>
e			<b>Domesting heating - Fossil fuels</b>					µg TEQ/t Ash
		1	High chlorine coal/waste/biomass co-fired stoves <i>LoC</i>	1,700 <i>L</i>	ND	NA	NA	5,000 <i>L</i>
		2	Coal/waste/biomass co-fired stoves <i>LoC</i>	200 <i>L</i>	ND	NA	NA	NA
		3	Coal fired stoves <i>LoC</i>	100 <i>M</i>	ND	NA	NA	5 <i>M</i>
		4	Peat fired stoves <i>LoC</i>	100 <i>M</i>	ND	NA	NA	NA
		4	Oil fired stoves <i>LoC</i>	10 <i>M</i>	ND	NA	NA	NA
		5	Natural gas fired stoves <i>LoC</i>	1.5 <i>M</i>	ND	NA	NA	NA

**Table III.4.4 Emission factors for group 4 – Production of Mineral Products**

Group	Cat.	Class	Source categories	Potential Release Route (µg TEQ/t)				
				Air	Water	Land	Product	Residue
<b>4</b>			<b>Production of Mineral Products</b>					
	<b>a</b>		<b>Cement kilns</b>					
		1	Shaft kilns <i>LoC</i>	5 ND <i>H</i>	NA	ND	ND	ND
		2	Old wet kilns, ESP temperature >300°C <i>LoC</i>	5 ND <i>H</i>	NA	ND	ND	ND
		3	Rotary kilns, ESP/FF temperature 200 to 300°C <i>LoC</i>	0.6 ND <i>H</i>	NA	ND	ND	ND
		4	Wet kilns, ESP/FF temperature <200°C and all types of dry kilns with preheater/precalciner, T<200°C <i>LoC</i>	0.05 ND <i>H</i>	NA	ND	ND	ND
	<b>b</b>		<b>Lime</b>					
		1	Cyclone/no dust control, contaminated or poor fuels <i>LoC</i>	10 ND <i>M</i>	NA	ND	ND	ND
		2	Good dust abatement <i>LoC</i>	0.07 ND <i>H</i>	NA	ND	ND	ND
	<b>c</b>		<b>Brick</b>					
		1	No emission abatement in place and using contaminated fuels <i>LoC</i>	0.2 NA <i>H</i>	NA	NA	0.06 <i>H</i>	0.02 <i>H</i>
		2	No emission abatement in place and using non-contaminated fuels; Emission abatement in place and using any kind of fuel; No emission abatement in place but state of the art process control <i>LoC</i>	0.02 NA <i>M</i>	NA	NA	0.006 <i>M</i>	0.002 <i>M</i>
	<b>d</b>		<b>Glass</b>					
		1	Cyclone/no dust control, contaminated or poor fuels <i>LoC</i>	0.2 NA <i>M</i>	NA	NA	ND	ND
		2	Good dust abatement <i>LoC</i>	0.015 NA <i>M</i>	NA	NA	ND	ND
	<b>e</b>		<b>Ceramics</b>					
		1	Cyclone/no dust control, contaminated or poor fuels <i>LoC</i>	0.2 NA <i>M</i>	NA	NA	ND	ND
		2	Good dust abatement <i>LoC</i>	0.02 NA <i>M</i>	NA	NA	ND	ND
	<b>f</b>		<b>Asphalt mixing</b>					
		1	Mixing plant with no gas cleaning	0.07 NA	NA	NA	ND	ND



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			LoC	M				
		2	Mixing plant with fabric filter, wet scrubber	0.007	NA	NA	ND	0.06
			LoC	M				M
	g		<b>Oil shale processing</b>					
		1	Thermal fractionation	ND	ND	ND	ND	ND
		2	Oil shale pyrolysis	0.003	NA	ND	0.07	2
			LoC	M			M	M

**Table III.4.5 Emission factors for group 5 – Transport**

Group	Cat.	Class	Source categories	Potential Release Route (µg TEQ/t)				
				Air	Water	Land	Product	Residue
<b>5</b>			<b>Transport</b>					
	<b>a</b>		<b>4-Stroke engines</b>					
		1	Leaded fuel <i>LoC</i>	2.2 <i>H</i>	NA	NA	NA	NA
		2	Unleaded gasoline without catalyst <i>LoC</i>	0.1 <i>M</i>	NA	NA	NA	NA
		3	Unleaded gasoline with catalyst <i>LoC</i>	0.001 <i>M</i>	NA	NA	NA	NA
		4	Ethanol with catalyst <i>LoC</i>	0.0007 <i>L</i>	NA	NA	NA	NA
	<b>b</b>		<b>2-Stroke engines</b>					
		1	Leaded fuel <i>LoC</i>	3.5 <i>L</i>	NA	NA	NA	NA
		2	Unleaded fuel <i>LoC</i>	2.5 <i>L</i>	NA	NA	NA	NA
	<b>c</b>		<b>Diesel engines</b>					
		1	Regular Diesel <i>LoC</i>	0.1 <i>M</i>	NA	NA	NA	ND
		2	Biodiesel <i>LoC</i>	0.07 <i>M</i>	NA	NA	NA	ND
	<b>d</b>		<b>Heavy oil fired engines</b>					
		1	All types <i>LoC</i>	2 <i>M</i>	NA	NA	NA	ND

**Table III.4.6 Emission factors for group 6 – Open Burning Processes**

Group	Cat.	Class	Source categories	Potential Release Route (µg TEQ/t)				
				Air	Water	Land	Product	Residue
<b>6</b>			<b>Open Burning Processes</b>					
	<b>a</b>		<b>Biomass burning</b>					
		1	Agricultural residue burning in the field of cereal and other crops stubble, impacted, poor burning conditions <i>LoC M</i>	30	ND	10	NA	NA
		2	Agricultural residue burning in the field of cereal and other crops stubble, not impacted <i>LoC M</i>	0.5	ND	0.05	NA	NA
		3	Sugarcane burning <i>LoC H</i>	4	ND	0.05	NA	NA
		4	Forest fires <i>LoC H</i>	1	ND	0.15	NA	NA
		5	Grassland and savannah fires <i>LoC H</i>	0.5	ND	0.15	NA	NA
	<b>b</b>		<b>Waste burning and accidental fires</b>					
		1	Fires at waste dumps (compacted, wet, high organic carbon content) <i>LoC M</i>	300	ND	10	NA	NA
		2	Accidental fires in houses, factories <i>LoC M</i>	400	ND	400	NA	NA
		3	Open burning of domestic waste <i>LoC M</i>	40	ND	1	NA	NA
		4	Accidental fires in vehicles (per vehicle) <i>LoC M</i>	100	ND	18	NA	NA
		5	Open burning of wood (construction/demolition) <i>LoC M</i>	60	ND	10	NA	NA

**Table III.4.7 Emission factors for group 7 – Production and Use of Chemicals and Consumer Goods**

Group	Cat.	Class	Source categories	Potential Release Route (µg TEQ/t)					
				Air	Water	Land	Product	Residue	
7	a	<b>Production and Use of Chemicals and Consumer Goods</b>	<b>Pulp and paper mills *</b>						
			<i>Boilers (per ton ADt pulp)</i>						
			1 Recovery boilers fueled with black liquor	0.03				ND	
			LoC	M					
			2 Power boilers fueled with sludge and/or biomass/bark	0.5				5	
			LoC	M			M		
			3 Power boilers fueled with salt-laden wood	13				228	
			LoC	M			M		
			<i>Acqueous discharges and products</i>						
		1 Kraft process, Cl <sub>2</sub> , non-wood, PCP-contaminated fibers		ND			30	ND	
		LoC				M			
		2 Kraft process, Cl <sub>2</sub>		4.5			10	4.5	
		LoC		M		M	M	M	
		3 Mixed technology		1.0			3	1.5	
		LoC		M		M	M	M	
		4 Sulfite process, Cl <sub>2</sub>		ND			1	ND	
		LoC				M			
		5 Kraft process, ClO <sub>2</sub>		0.06			0.5	0.2	
		LoC		M		M	M	M	
		6 Sulfite process, either ClO <sub>2</sub> or TCF		ND			0.1	ND	
		LoC				M			
		7 Thermo-mechanical process		ND			1.0	ND	
		LoC				M			
8 Paper recycling with contaminated waste paper		ND			10	ND			
LoC				M					
9 Paper recycling with modern paper		ND			3	ND			
LoC				M					
b	<b>Chlorinated Inorganic Chemicals</b>	<i>Elemental chlorine production (per ton ECU)</i>							
		1 Chlor-alkali production using graphite anodes	ND	ND	ND	ND	1,000		
		LoC				L			
		2 Chlor-alkali production using titanium electrodes							
		2a Low-End Technologies	ND	17	ND	ND	27		
		LoC		L			L		
2b Mid-Range Technologies	ND	1.7	ND	ND	1.7				
LoC		L			L				
2c High-End Technologies	ND	0.002	ND	ND	0.3				

		LoC	L		L	
<b>c</b>	<b>Chlorinated Aliphatic Chemicals</b>					
	<i>ECD/VCM and EDC/VCM/PVC vent and liquid-vent combustors (per ton VCM)</i>					
	Low-End Technologies	5				
	LoC	L				
	Mid-Range Technologies	0.5				
	LoC	L				
	High-End Technologies	0.05				
	LoC	L				
	<i>ECD/VCM and EDC/VCM/PVC spent catalyst from facilities utilizing a fixed-bed oxychlorination catalyst (per ton EDC)</i>					
	Low-End Technologies				8	
	LoC				L	
	Mid-Range Technologies				0.85	
	LoC				L	
	High-End Technologies*				0.02	
	LoC				L	
	<i>ECD/VCM and EDC/VCM/PVC production processes (per ton EDC)</i>					
	1 Low-End Technologies					
	With fixed-bed oxychlorination catalyst		25 NA		2	0.75
	With fluidized-bed oxychlorination catalyst		25 NA		2	4
	LoC		L		L	L
	2 Mid-Range Technologies					
	With fixed-bed oxychlorination catalyst		2.5 NA		0.2	0.2
	With fluidized-bed oxychlorination catalyst		2.5 NA		0.2	2
	LoC		L		L	L
3 High-End Technologies*						
With fixed-bed oxychlorination catalyst		0.5 NA		0.006	0.095	
With fluidized-bed oxychlorination catalyst		0.5 NA		0.006	0.4	
LoC		L		L	L	
<i>PVC only (per ton PVC product)</i>						
1 Low-End Technologies		1	0.03 NA	ND	0.095	
LoC		L	L		L	
2 Mid-Range Technologies		0.1	0.003 NA	ND	0.06	
LoC		L	L		L	
3 High-End Technologies*		0.021	0.0003 NA	NA	0.005	
LoC		L	L		L	
<b>d</b>	<b>Chlorinated Aromatic Chemicals (per ton product)</b>					
	<i>Chlorobenzenes</i>					
	1 1,4-Dichlorobenzene	ND	ND	NA	39 ND	
LoC				M		
	<i>PCB</i>					
1	Low chlorinated, Clophen A30, Aroclor 1242				15,000	

		LoC				M	
2	Medium chlorinated, Clophen A40, Aroclor 1248					70,000	
		LoC				M	
3	Medium chlorinated, Clophen A50, Aroclor 1254					300,000	
		LoC				M	
4	High chlorinated, Clophen A60, Aroclor 1260					1,500,000	
		LoC				M	
	<i>PCP and PCP-Na</i>						
1	PCP	ND	ND	ND		634,000	ND
		LoC				M	
2	PCP-Na	ND	ND	ND		12,500	ND
		LoC				M	
	<i>2,4,5-T and 2,4,5-TCP</i>						
1	2,4,5-T	ND	ND	ND		7,000	ND
		LoC				M	
2	2,4,5-TCP	ND	ND	ND		700	ND
		LoC				M	
	<i>Chloronitrofen (CNP)</i>						
1	Old technologies	ND	ND	ND		9,200,000	ND
		LoC				M	
2	New technologies	ND	ND	ND		4,500	ND
		LoC				M	
	<i>Pentachloronitrobenzene (PCNB)</i>						
1	Low-End Technologies	ND	ND	ND		5,600	ND
		LoC				M	
2	Mid-Range Technologies	ND	ND	ND		2,600	ND
		LoC				M	
3	High-End Technologies	ND	ND	ND		260	ND
		LoC				M	
	<i>2,4-D and derivatives</i>						
1	Low-End Technologies	ND	ND	ND		5,688	ND
		LoC				M	
2	Mid-Range Technologies	ND	ND	ND		170	ND
		LoC				M	
3	High-End Technologies	ND	ND	ND		0.1	ND
		LoC				M	
	<i>Chlorinated Paraffins</i>						
1	Low-End Technologies	ND	ND	ND		ND	ND
		LoC				M	
2	Mid-Range Technologies	ND	ND	ND		500	ND
		LoC				M	
3	High-End Technologies	ND	ND	ND		140	ND
		LoC				M	
	<i>P-chloranil</i>						
1	Direct chlorination of phenol	ND	ND	ND		400,000	ND
		LoC				M	

	2	Chlorination of hydroquinone with minimal purification	ND	ND	ND	1,500,000	ND
		LoC				M	
	3	Chlorination of hydroquinone with moderate purification	ND	ND	ND	26,000	ND
		LoC				M	
	4	Chlorination of hydroquinone with advanced purification	ND	ND	ND	150	ND
		LoC				M	
		<i>Phthalocyanine dyes and pigments</i>					
	1	Phthalocyanine copper	ND	ND	ND	70	ND
		LoC				M	
	2	Phthalocyanine green	ND	ND	ND	1,400	ND
		LoC				M	
		<i>Dioxazine dyes and pigments</i>					
	1	Blue 106	ND	ND	ND	35,000	ND
		LoC				M	
	2	Blue 108	ND	ND	ND	100	ND
		LoC				M	
	3	Violet 23	ND	ND	ND	12,000	ND
		LoC				M	
		<i>Triclosan</i>					
	1	Low-End Technologies	ND	ND	ND	1,700	82,000
		LoC				M	M
	2	Mid-Range Technologies	ND	ND	ND	60	ND
		LoC				M	
	3	High-End Technologies	ND	ND	ND	3	ND
		LoC				M	
e		<b>Other Chlorinated and Non-Chlorinated Chemicals (per ton product)</b> <i>TiCl<sub>4</sub> and TiO<sub>2</sub></i>					
	1	Low-End Technologies	ND	0.2	ND	0	42
		LoC		M		M	M
	2	Mid-Range Technologies	ND	0.001	ND	0	8
		LoC		M		M	M
		<i>Caprolactam</i>					
	1	Caprolactam		0.5 (pg 0.00035 TEQ/L)	ND	ND	ND
		LoC		M	M		
f		<b>Petroleum refining</b>					
	1	Flares (per TJ fuel burned)	0.25	NA	NA	NA	ND
		LoC	M				
		<i>Production processes (per ton oil)</i>					
	1	Catalytic reforming unit	0.02	NA	NA	NA	14 (µg TEQ/t residue)
		LoC	M				M

		2	Coking unit	LoC	0.4 M	NA	NA	NA	ND
		3	Refinery-wide wastewater treatment	LoC	ND	5 (pg TEQ/L) M	ND	ND	ND
<b>g</b>	<b>Textile plants</b>								
	1	Low-End Technologies		LoC	ND	ND	ND	100 L	ND
	2	Mid-Range, non-BAT Technologies		LoC	ND	ND	ND	0.1 L	ND
		3	High-End, BAT Technologies		NA	NA	NA	NA	NA
<b>h</b>	<b>Leather plants</b>								
	1	Low-End Technologies		LoC	NA	ND	ND	1,000 L	ND
		2	Mid-Range Technologies	LoC	NA	ND	ND	10 L	ND

\* Releases to residues from EDC/VCM, EDC/VCM/PVC and PVC-only facilities with high-end technologies (waste water treatment solids and/or spent catalyst) only if solids are NOT incinerated



**Table III.4.8 Emission factors for group 8 – Miscellaneous**

Group	Cat.	Class	Source categories	Potential Release Route (µg TEQ/t)				
				Air	Water	Land	Product	Residue
<b>8</b>			<b>Miscellaneous</b>					
	<b>a</b>		<b>Drying of biomass</b>					
		1	Highly contaminated fuel (PCP treated)	10	NA	ND	0.5	2,000
			<i>LoC</i>	<i>L</i>			<i>L</i>	<i>L</i>
		2	Moderately contaminated fuel	0.1	NA	ND	0.1	20
			<i>LoC</i>	<i>L</i>			<i>L</i>	<i>L</i>
		3	Clean fuel	0.01	NA	ND	0.1	5
			<i>LoC</i>	<i>L</i>			<i>L</i>	<i>L</i>
	<b>b</b>		<b>Crematoria</b>					
		1	No control (per cremation)	90	NA	NA	NA	ND
			<i>LoC</i>	<i>H</i>				
		2	Medium control or open air cremations (per cremation)	10	NA	NA	NA	2.5
			<i>LoC</i>	<i>M</i>				<i>M</i>
		3	Optimal control (per cremation)	0.4	NA	NA	NA	2.5
			<i>LoC</i>	<i>L</i>				<i>L</i>
	<b>c</b>		<b>Smoke houses</b>					
		1	Contaminated fuels	50	NA	ND	ND	2,000
			<i>LoC</i>	<i>L</i>				<i>L</i>
		2	Clean fuels, no afterburner	6	NA	ND	ND	20
			<i>LoC</i>	<i>L</i>				<i>L</i>
		3	Clean fuels, afterburner	0.6	NA	ND	ND	20
			<i>LoC</i>	<i>L</i>				<i>L</i>
	<b>d</b>		<b>Dry cleaning</b>					
		1	Heavy textiles, PCP-treated, etc.	NA	NA	NA	NA	3,000
			<i>LoC</i>					<i>L</i>
		2	Normal textiles	NA	NA	NA	NA	50
			<i>LoC</i>					<i>L</i>
	<b>e</b>		<b>Tobacco smoking</b>					
		1	Cigar (per million cigars)	0.3	NA	NA	NA	0.3
			<i>LoC</i>	<i>L</i>				<i>L</i>
		2	Cigarette (per million cigarettes)	0.1	NA	NA	NA	0.1
			<i>LoC</i>	<i>L</i>				<i>L</i>

**Table III.4.9 Emission factors for group 9 – Disposal and Landfill**

Group	Cat.	Class	Source categories	Potential Release Route (µg TEQ/t)				
				Air	Water	Land	Product	Residue
<b>9</b>			<b>Disposal and Landfill</b>					
	<b>a</b>		<b>Landfills, Waste Dumps and Landfill Mining</b>					
		<b>1</b>	<b>Hazardous wastes</b>	NA <i>LoC</i>	<b>5</b> <i>L</i>	NA	NA	NA
		<b>2</b>	<b>Mixed wastes</b>	NA <i>LoC</i>	<b>0.5</b> <i>L</i>	NA	NA	<b>50</b> <i>L</i>
		<b>3</b>	<b>Domestic wastes</b>	NA <i>LoC</i>	<b>0.05</b> <i>L</i>	NA	NA	<b>5</b> <i>L</i>
	<b>b</b>		<b>Sewage and sewage treatment (per ton d.m.*)</b> <b>* for water releases, units are in pg TEQ/L</b>					
		<b>1</b>	<b>Mixed domestic and specific industrial inputs</b>					
			No sludge removal	NA	<b>10</b>	NA	NA	<b>NA</b>
			With sludge removal	NA <i>LoC</i>	<b>1</b> <i>H</i>	NA	NA	<b>200</b> <i>H</i>
		<b>2</b>	<b>Urban and industrial inputs</b>					
			No sludge removal	NA	<b>1</b>	NA	NA	<b>NA</b>
			With sludge removal	NA <i>LoC</i>	<b>0.2</b> <i>H</i>	NA	NA	<b>20</b> <i>H</i>
		<b>3</b>	<b>Domestic inputs</b>					
			No sludge removal	NA	<b>0.04</b>	NA	NA	<b>NA</b>
			With sludge removal	NA <i>LoC</i>	<b>0.04</b> <i>H</i>	NA	NA	<b>4</b> <i>H</i>
	<b>c</b>		<b>Open water dumping (per m<sup>3</sup>)</b>					
		<b>1</b>	Mixed domestic and industrial wastewater	NA <i>LoC</i>	0.005 <i>L</i>	NA	NA	NA
		<b>2</b>	Urban and peri-urban wastewater	NA <i>LoC</i>	0.0002 <i>L</i>	NA	NA	NA
		<b>3</b>	Remote environments	NA <i>LoC</i>	0.0001 <i>L</i>	NA	NA	NA
	<b>d</b>		<b>Composting (per ton d.m.)</b>					
		<b>1</b>	<b>Organic wastes separated from mixed wastes</b>	NA <i>LoC</i>	NA	NA	<b>50</b> <i>H</i>	NA
		<b>2</b>	<b>Clean compost</b>	NA <i>LoC</i>	NA	NA	<b>5</b> <i>H</i>	NA
	<b>e</b>		<b>Waste oil disposal</b>					
		<b>1</b>	All fractions	ND	ND	ND	ND	ND

**Table III.4.10 Emission factors for group 10 – Contaminated Sites and Hotspots**

Group	Cat.	Class	Source categories	Product (µg TEQ/t)
<b>10</b>			<b>Contaminated Sites and Hotspots</b>	
	<b>a</b>		<b>Production sites of chlorine</b>	
		1	Chlor-alkali production	
		2	Leblanc process and associated chlorine/bleach production	
	<b>b</b>		<b>Production sites of chlorinated organics</b>	
		1	Production sites of chlorophenol	
		2	Former lindane production where HCH waste isomers have been recycled	
		3	Former production sites of other chemicals suspected to contain PCDD/PCDF	
		4	Production sites of chlorinated solvents and other "HCB waste"	
		5	(Former) PCB and PCB-containing materials/equipment production	
	<b>c</b>		<b>Application sites of PCDD/PCDF containing pesticides and chemicals</b>	
	<b>d</b>		<b>Timber manufacture and treatment sites</b>	
	<b>e</b>		<b>Textile and leather factories</b>	
	<b>f</b>		<b>Use of PCB</b>	
	<b>g</b>		<b>Use of chlorine for production of metals and inorganic chemicals</b>	
	<b>h</b>		<b>Waste incinerators</b>	
	<b>i</b>		<b>Metal industries</b>	
	<b>j</b>		<b>Fire accidents</b>	
	<b>k</b>		<b>Dredging of sediments and contaminated flood plains</b>	
	<b>l</b>		<b>Dumps of wastes/residues from groups 1-9</b>	
	<b>m</b>		<b>Kaolin or ball clay sites</b>	

## Annex 5 Reporting under the Article 15 of the Stockholm Convention

Source categories of releases of unintentional POPs under the Stockholm Convention are listed in Annex C Part II and Part III to the Convention. These source categories are also among those considered in the Toolkit, where they are placed into ten source groups to facilitate elaboration and reporting of POPs releases. The standard format for reporting PCDD/PCDF releases through national reports under Article 15 is given in table III.5.1 below.

Some countries also report POPs releases to air and a number of other pollutants under the UNECE Convention on Long-Range Transboundary Air Pollution (CLRTAP). For these countries, the correspondence between source categorization under CLRTAP, according to the Guidelines for Reporting Emission Data under the Convention on Long-Range Transboundary Air Pollution (ECE/EB.AIR/2008/4) and the source categories of the Stockholm Convention is presented in table III.5.2 below. Under the CLRTAP guidelines, sources are categorized according to the Common Reporting Format (CFR), which is a standardized format for reporting national emissions under the United Nations Framework Convention on Climate Change (UNFCCC) and CLRTAP. Within the CFR a standardized Nomenclature for Reporting (NFR) lists and classifies a number of source categories and sub-sectors by codes.

**Table III.5.1 Format for reporting PCDD/PCDF releases in the national reports under Article 15 of the Stockholm Convention**

SOURCE GROUP	ANNUAL RELEASES OF PCDD-PCDF (G TEQ/A)				
	YEAR				
	AIR	WATER	LAND	PRODUCT	RESIDUE
Waste incineration					
Ferrous and non-ferrous metal production					
Heat and power generation					
Production of mineral products					
Transportation					
Open burning processes					
Production of chemicals and consumer goods					
Waste disposal					
Miscellaneous					
<b>TOTAL</b>	0	0	0	0	0

**Table III.5.2 Transposition of source categorization between Annex C of the Stockholm Convention, SNAP 97 and NFR.**

UNEP Dioxin/Furan Toolkit	Stockholm Convention Annex C	SNAP 97	NFR
<b>1. Waste incineration</b>			
1a. Municipal solid waste incineration	Part II (a)	090201	6C
1b. Hazardous waste incineration	Part II (a) Part II (b)	090202, 090208	6C
1c. Medical waste incineration	Part II (a)	090207	6C
1d. Light-fraction shredder waste incineration	Part II (a)	090202	6C
1e. Sewage sludge incineration	Part II (a)	090205	6C
1f. Waste wood and waste biomass Incineration	Part II (a)	090201, 090202	6C
1g. Destruction of animal carcasses	Part III (i)	090902	6C
<b>2. Ferrous and non-ferrous metal production</b>			
2a. Iron ore sintering	Part II (d)(ii)	030301	1A2a
2b. Coke production	Part III (b)	010406	1A1c
2c. Iron and steel production	Part III (b)	030203, 040205, 040206, 040207	1A2a 2C1
Foundries	Part III (b)	030303	1A2a
2d. Copper production	Part II (d) (i)	030306, 030309	1A2b, 2C5a
2e. Aluminum production	Part II (d)(iii)	030310 030322, 040301	1A2b 2C3
2f. Lead production	Part III (b)	030304, 030307	1A2b, 2C5b
2g. Zinc production	Part II (d)(iv)	030305, 030308, 040309	1A2b, 2C5d
2h. Brass and bronze production	Part III (b)	030326, 040309	1A2b
2i. Magnesium production	Part III (b)	030323	1A2b
2j. Other non-ferrous metal production	Part III (b)	030326, 040309	1A2b, 2C5e
2k. Shredders	Part III (k)		
2l. Thermal wire reclamation	Part III (l)	030307, 030309	1A2b
UNEP Dioxin/Furan Toolkit	Stockholm Convention Annex C	SNAP 97	NFR
<b>3. Power generation and heating/cooking</b>			

3a. Fossil fuel power plants	Part III (c)	0101, 0102, 0201, 0202	1A1a, 1A1b, 1A1c, 1A2a, 1A2b, 1A2c, 1A2d, 1A2e, 1A2f, 1A4a,1A4c, 1A5a
3b. Biomass power plants	Part III (e)	0101, 0102, 0201, 0202,	1A1a, 1A1b, 1A1c, 1A2a, 1A2b, 1A2c, 1A2d, 1A2e, 1A2f, 1A4a,1A4c, 1A5a
3c. Landfill, biogas combustion	Part III (e)	091006	6D
3d. Household heating and cooking (biomass)	Part III (c)	020205	1A4b
3e. Domestic heating (fossil fuels)	Part III (c)	020205	1A4b
<b>4. Production of mineral products</b>			
4a. Cement production	Part III (d)	030311	1A2f
4b. Lime production	Part III (d)	030312	1A2f
4f. Asphalt mixing	Part III (d)	030313	1A2f
4d. Glass production	Part III (d)	030314- 030318	1A2f
4e. Ceramic production	Part III (d)	030320	1A2f
4c. Brick production	Part III (d)	030319	1A2f
<b>5. Transport</b>			
5a. 4 –Stroke engines	Part III (h)	0701, 0702, 0703,0704,07 05	1A3b
5b. 2- Stroke engines	Part III (h)	0704,0705	1A3b
5c. Diesel engines	Part III (h)	0701, 0702, 0703, 0801, 0802, 0806, 0808	1A3b, 1A3c, 1A2f, 1A4a, 1A4b, 1A4c, 1A5b,
5d. Heavy oil fired engines	Part III (h)	080402, 080403, 080404, 080304	1A3d, 1A4c, 1A5b
<b>UNEP Dioxin/Furan Toolkit</b>	<b>Stockholm Convention Annex C</b>	<b>SNAP 97</b>	<b>NFR</b>
<b>6. Open burning</b>			

6a. Biomass burning: Forest fires	Part III (a)	110301, 110302	11B
Savanah burning			4E
Agriculture residue burning			4F
6b. Waste burning, accidental fire	Part III (a)	0907	6D
<b>7. Production and use of chemicals and consumer goods</b>			
7a. Pulp and paper production	Part II (c)	040602-04	2D1
7b. Chlorinated inorganic chemicals	Part III (f)	0405	2B5
7c. Chlorinated aliphatic chemicals	Part III (f)	0405	2B5
7d. Chlorinated aromatic chemicals	Part III (f)	0405	2B5
7e. Other chlorinated and non-chlorinated chemicals	Part III (f)	0405	2B5
7f. Petroleum industry	Part III (f)	0401	1B2aiv
7g. Textile production	Part III (j)	060313	3c
7h. Leather refining	Part III (j)	060314	3c
<b>8. Miscellaneous</b>			
8a. Drying of biomass			
8b. Crematoria	Part III (g)	090901	6C
8c. Smoke houses			
8d. Dry cleaning	Part III (f)	060202	3B2
8e. Tobacco smoking			
<b>9. Disposal</b>			
9a. Landfills and waste dumps		090401, 090402	6A
9b. Sewage and sewage treatment		091001, 091002	6B
9c. Open water dumping		091001	6B
9d. Composting		091005	6D
9e. Waste oil treatment	Part III (m)	091008	6D
<b>UNEP Dioxin/Furan Toolkit</b>	<b>SC Article 6</b>	<b>SNAP 97</b>	<b>NFR</b>
<b>10. Identification of potential hotspots</b>			
10a. Production sites of chlorinated organics	Para 1 (e)		
10b. Production sites of chlorine	Para 1 (e)		
10c. Formulation sites of chlorinated phenols	Para 1 (e)		
10d. Application sites of chlorinated phenols	Para 1 (e)		
10e. Timber manufacture and treatment sites	Para 1 (e)		
10f. PCBs filled transformers and capacitors	Para 1 (e)	060507	2F

10g. Dumps of wastes/residues from groups 1-9	Para 1 (e)	090401, 090402	6A
10h. Sites of relevant accidents	Para 1 (e)		
10e. Dredging of sediments	Para 1 (e)		
10j. Kaolinite or ball clay sites	Para 1 (e)		



## Annex 6 Usage of units in air emissions

When reporting air concentrations care must be taken with respect to the base units given. The following definitions apply:

$m^3$	Cubic meter: is the SI unit of volume and may be used to express the volume of any substance, whether solid, liquid, or gas.
$Nm^3$	Normal cubic meter: refers to the volume of any gas at 0°C and 1 atm (101.325 kPa).  In European countries and for emissions from municipal waste incinerators (also co-combustion of waste): $Nm^3$ is defined at the following conditions: 101.325 kPa (= 1 atm), 273.15 K, dry gas, and 11% oxygen. For emissions from other types of combustion/thermal plants, there is no requirement to normalize to 11% oxygen.
$Rm^3$ in Canada:	Reference cubic meter. When using R, the conditions are 25°C, 1 atm, dry. The need for oxygen correction should be explicitly stated, although it sometimes is not. The Canada-wide standard utilizes are correction to 11% oxygen for incinerators and coastal pulp and paper mill boilers burning salt-laden wood residue. For others sectors such as sinter plants, they have decided to use no oxygen correction.
$Sm^3$ in U.S.A.:	Is the dry standard cubic meter (represented as dscm) at 1 atmosphere of pressure and 20 degrees Celsius (68 degrees Fahrenheit). The contaminant concentration is corrected to some standard percent oxygen or carbon dioxide in the combustion gases, usually 7% oxygen and 12% carbon dioxide.

## Annex 7 Per capita/GDP emissions

The Toolkit has been used by many countries to develop their national release inventories as required by Article 5 or Article 15 of the Convention. Through its structure for reporting, *i.e.*, ten source categories and five release vectors, it is possible to gain further insight into the global situation as to the sources of PCDD/PCDF releases. In 2011, 68 national inventories have been assessed and the quantitative releases have been correlated to geographic, demographic and source-specific information. The results for the total releases and according to the release vector are shown in table III.7.1; most countries have used the emission factors from the 2<sup>nd</sup> edition of the Toolkit (2005).

**Table III.7.1 Summary table of PCDD/PCDF releases according to release vector (releases in g TEQ/a)**

PCDD/PCDF Releases (g TEQ per year)				
Air	Water	Land	Product	Residue
26,400	1,200	6,000	4,800	19,800
<b>45%</b>	<b>2%</b>	<b>11%</b>	<b>8%</b>	<b>34%</b>
<b>Grand total (ca.)</b>		<b>58,500</b>		

The 68 countries used in this assessment are the following (ISO 3-digit code):

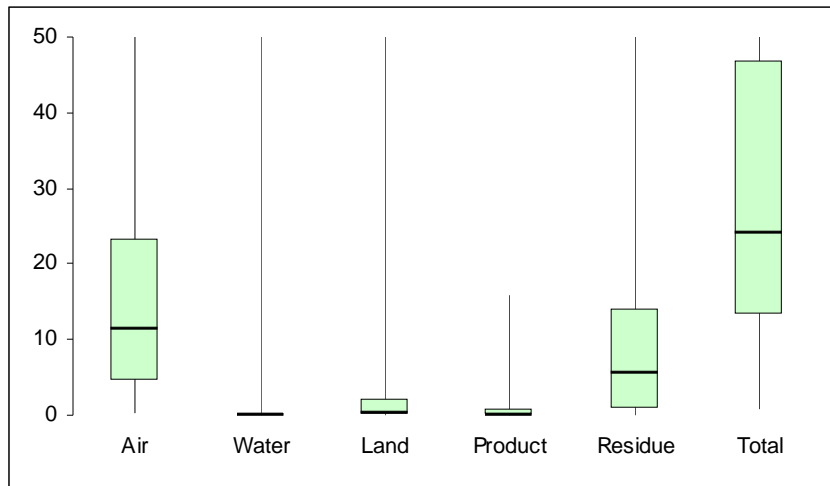
ALB, ARG, ARM, AUS, AZE, BLR, BEN, BRN, BFA, BDI, KHM, CHL, CHN, HKG, COL, CIV, HRV, CUB, DJI, ECU, EST, ETH, FJI, GAB, GMB, GHA, GER, IND, IDN, IRN, JOR, KEN, LAO, LBN, LBR, LTU, MKD, MDG, MLI, MUS, MDA, MAR, NPL, NZL, NIC, NIG, NIU, PAN, PRY, PER, PHL, POR, ROU, SAM, SRB, SYC, SVN, LKA, SDN, SYR, TJK, TZA, THA, TGO, TUN, URY, VNM, ZMB (Fiedler *et al.* 2012).

The combined population is 3.80 billion, and the reference years for the inventories ranged over ten years, from 1999 (Philippines) to 2009 (India). Table III.7.2 shows the releases on a *per capita* basis taking into account the estimated release for each vector and the combined five vectors (total releases) for the population of the respective year.

**Table III.7.2 PCDD/PCDF releases *per capita* and year for each release vector and total ( $\mu\text{g}$  TEQ per person per year)**

	Air	Water	Land	Product	Residue	Total
Mean	21	4.6	3.4	1.1	10	40
Median	11	0.05	0.36	0.11	5.6	24
Minimum	0.20	0.0	0.0	0.0	0.0	0.88
Maximum	181	176	65	16	77	259
Count	68	68	68	68	68	68

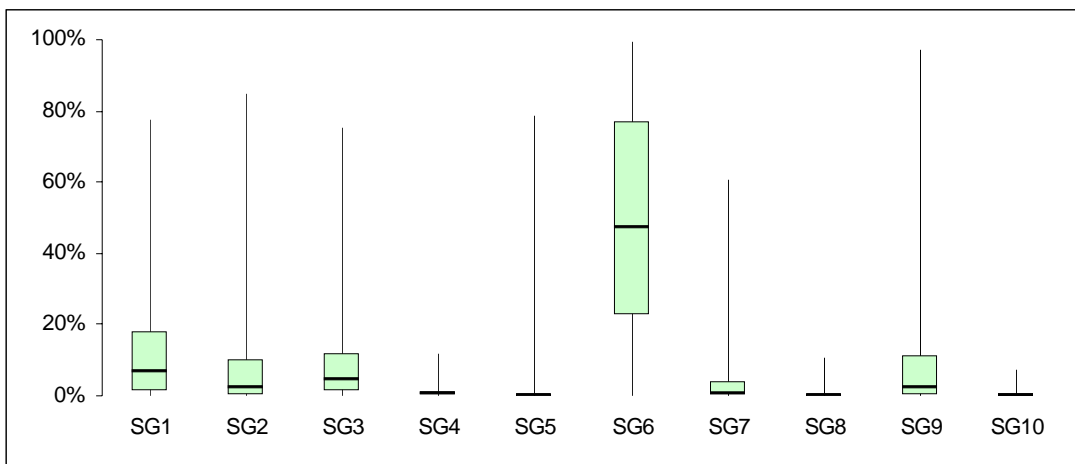
The graphical sketch is shown in Figure III.7.1.



**Figure III.7.1 Graphical sketch for PCDD/PCDF releases per and per year ( $\mu\text{g TEQ}$  per person per year)**

The weighting of the source groups is shown in Figure III.7.2. It can be seen that the most important source groups across 67 inventories are as follows:

1. SG6 (open burning of biomass and waste) = 49%
2. SG1 (incineration of waste) = 14%
3. SG3 (conversion of energy) = 10%
4. SG2 (production of metals) = 9%



**Figure III.7.2 Statistical evaluation of importance of source groups (n=67)**

The following two figures present the total annual releases *per country* (Figure III.7.3) and the annual releases to air *per country* (Figure III.7.4). The contribution from each of the ten source groups to the total annual releases are shown in Figure III.7.5 and III.7.6.

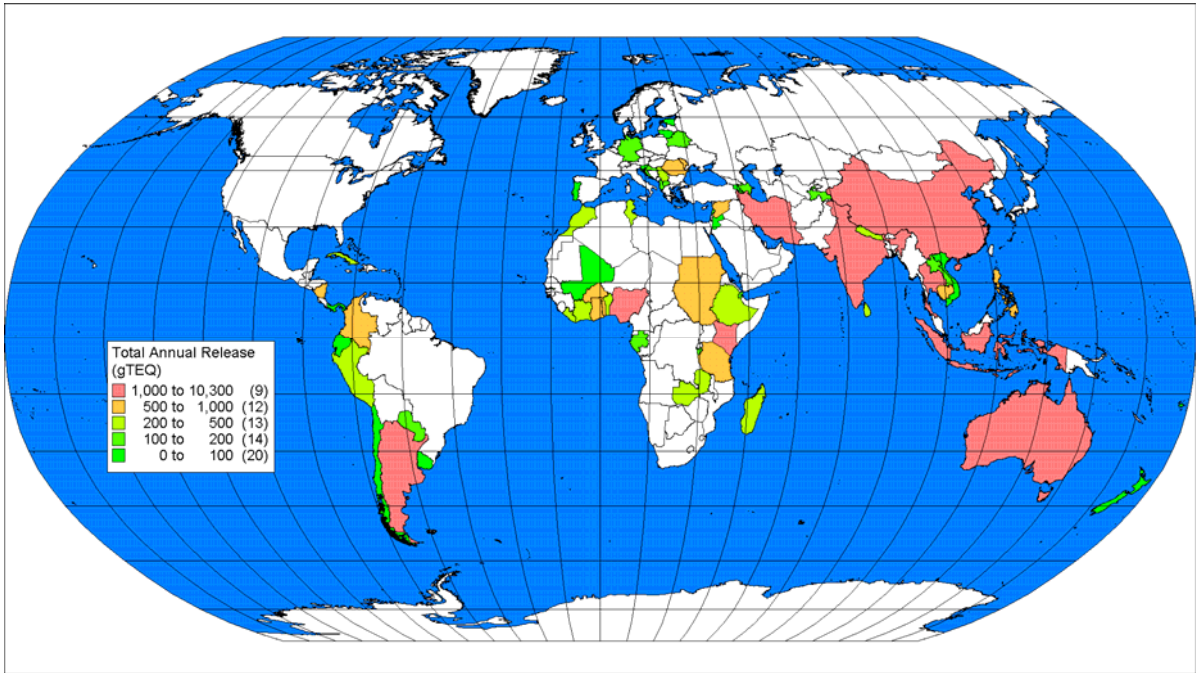


Figure III.7.3 Total annual release per country (g TEQ/a)

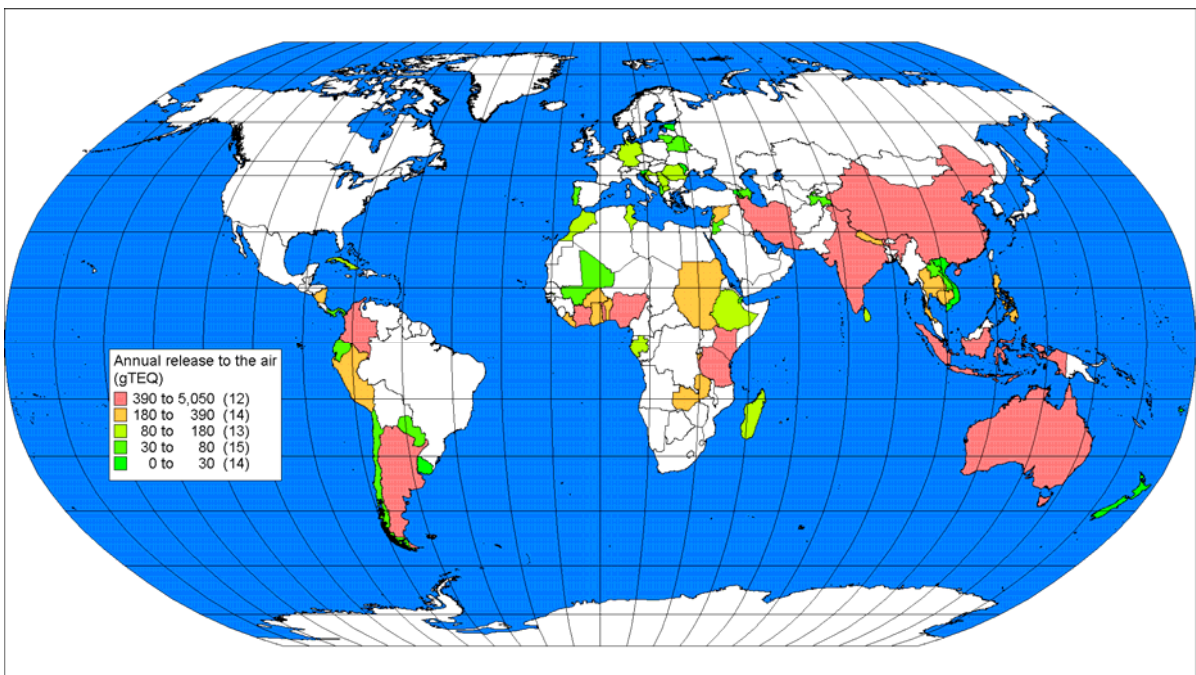


Figure III.7.4 Total annual release to air per country (g TEQ/a)

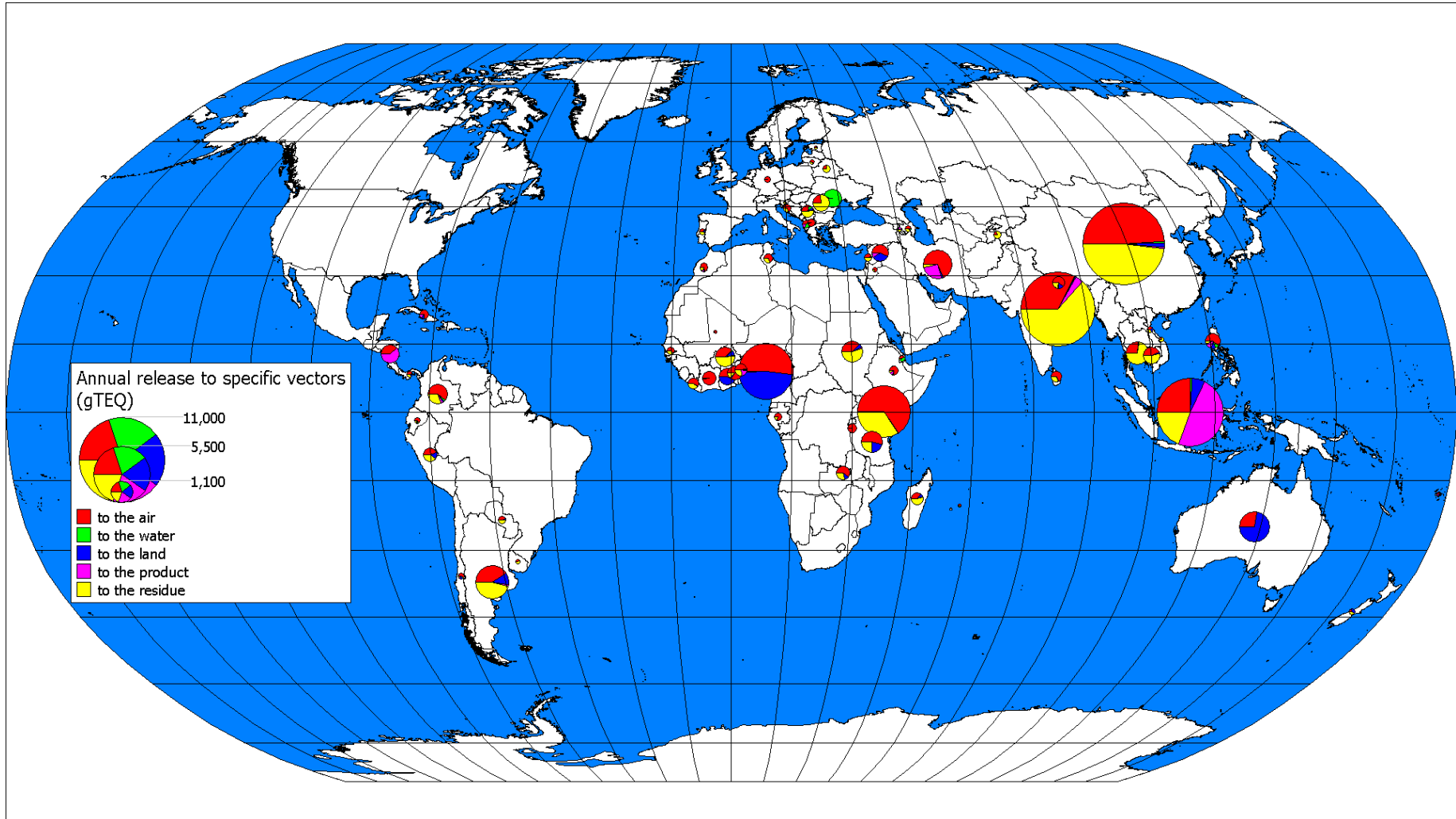


Figure III.7.5 Total annual release per country and vector (g TEQ/a)

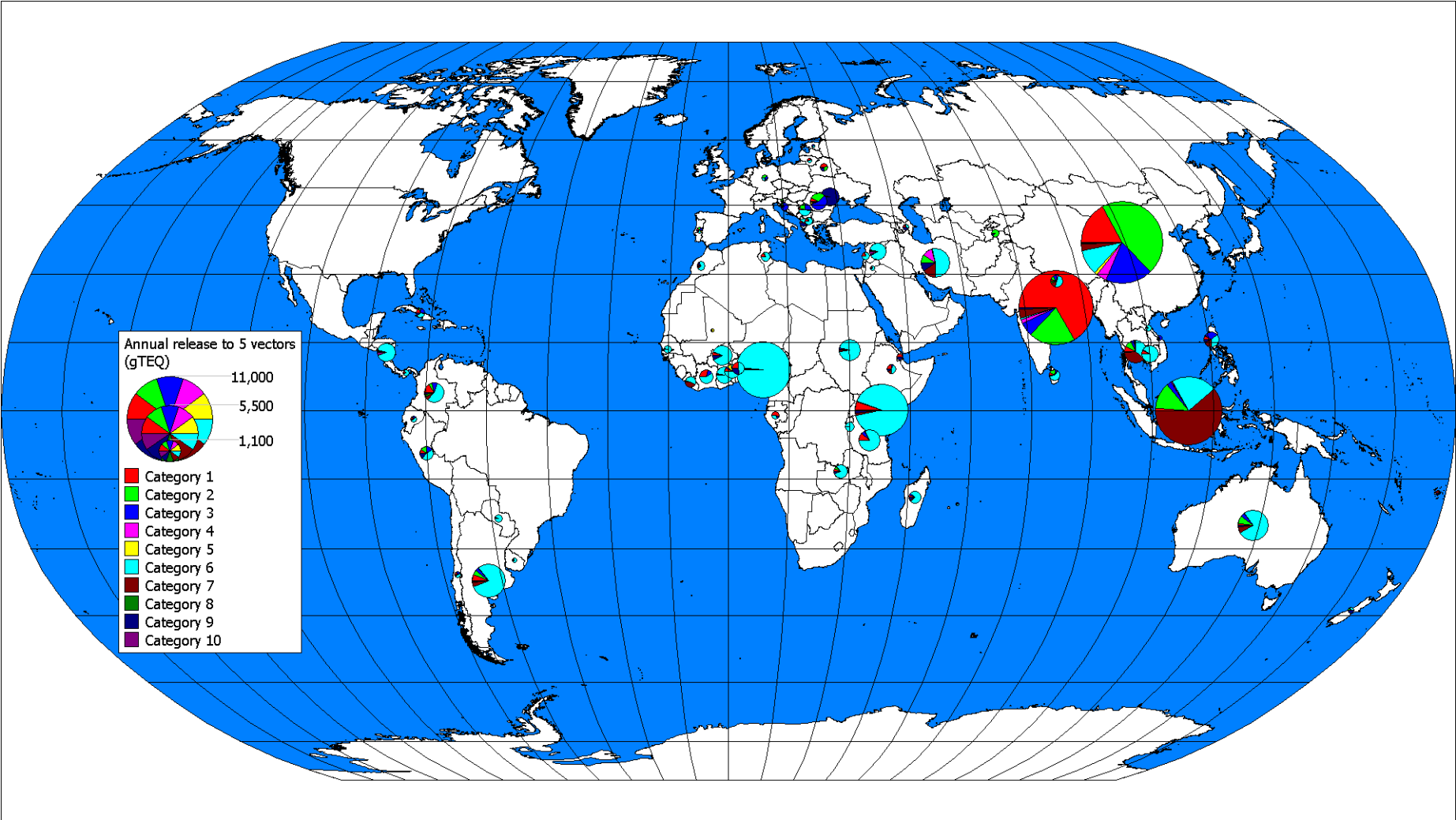


Figure III.7.6 Total annual release per country and source group (g TEQ/a)



The annual releases on population basis for the total releases are shown in Figure III.7.7 and to air in Figure III.7.8.

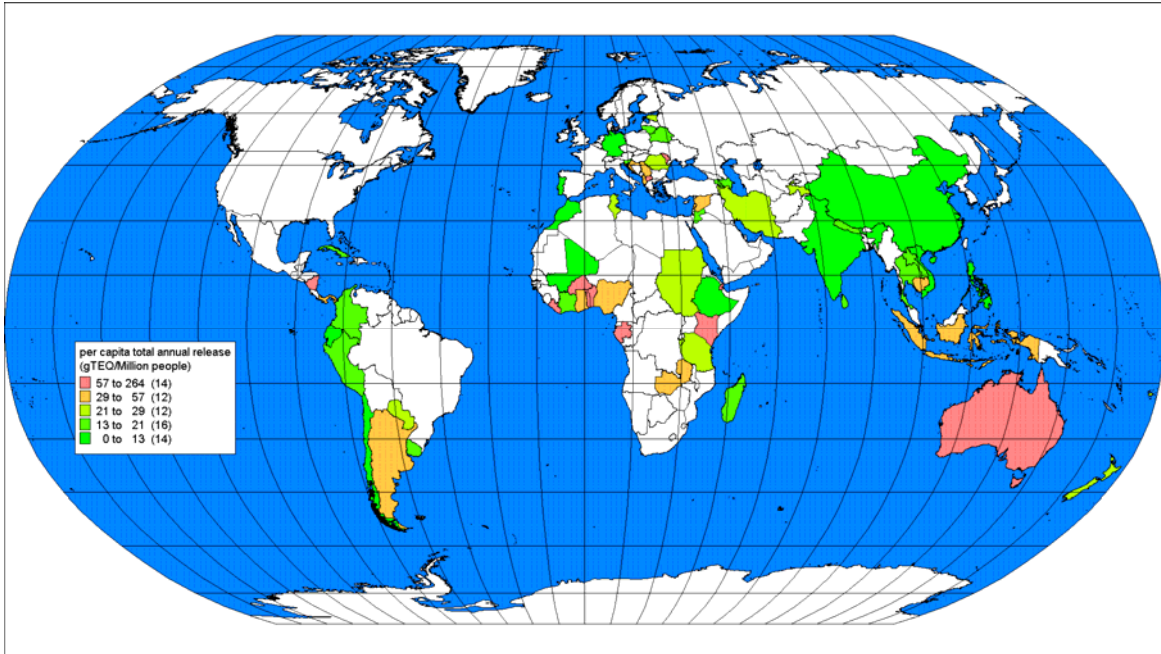


Figure III.7.7 Per capita total annual release ( $\mu\text{g TEQ/a}$ )

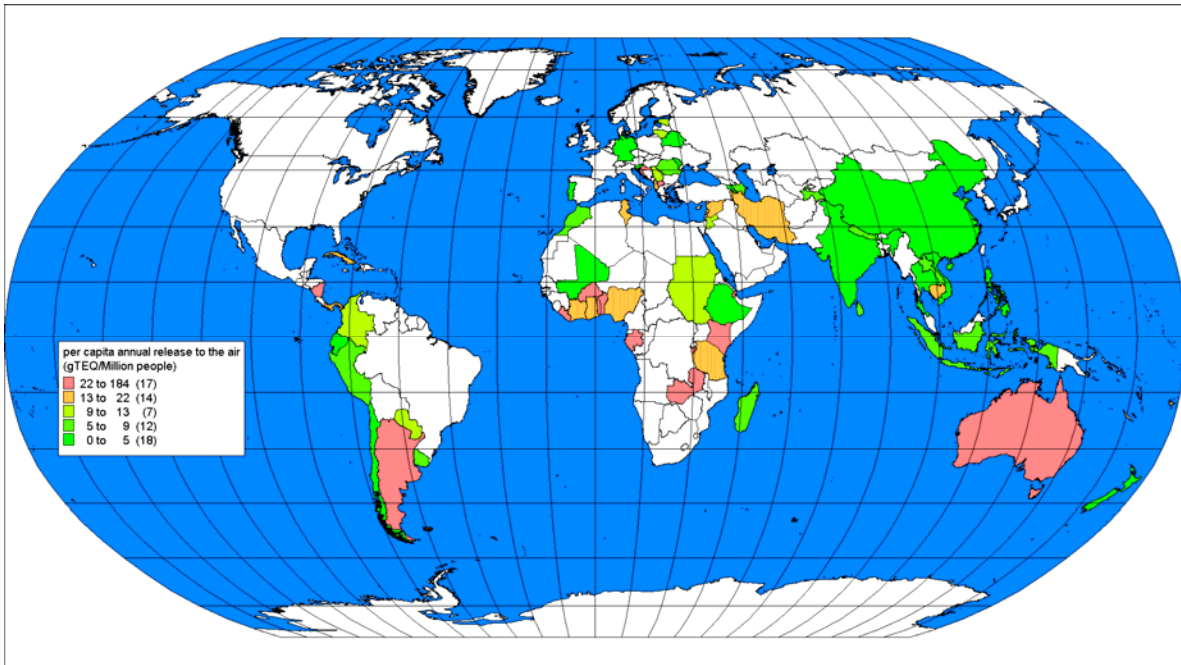


Figure III.7.8 Per capita annual release to air ( $\mu\text{g TEQ/a}$ )

Finally, the releases per unit area ( $\text{km}^2$ ) is shown in Figure III.7.9 and based on *per capita* gross domestic product in Figure III.7.10.

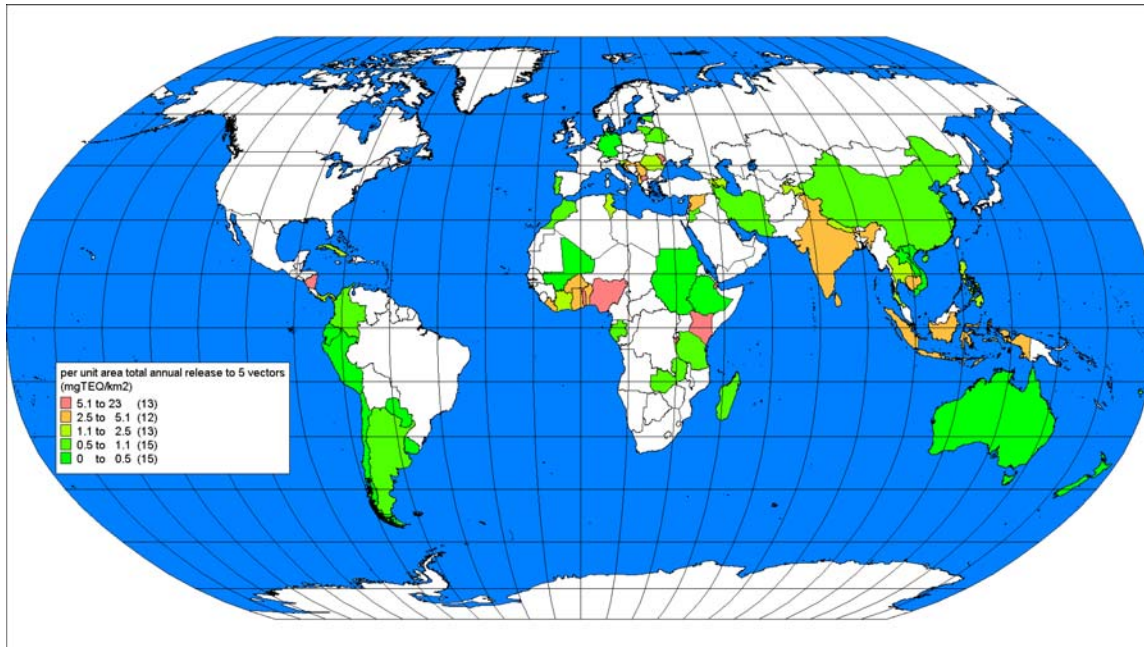


Figure III.7.9 Total annual release per square kilometer ( $\mu\text{g TEQ}/\text{km}^2$ )

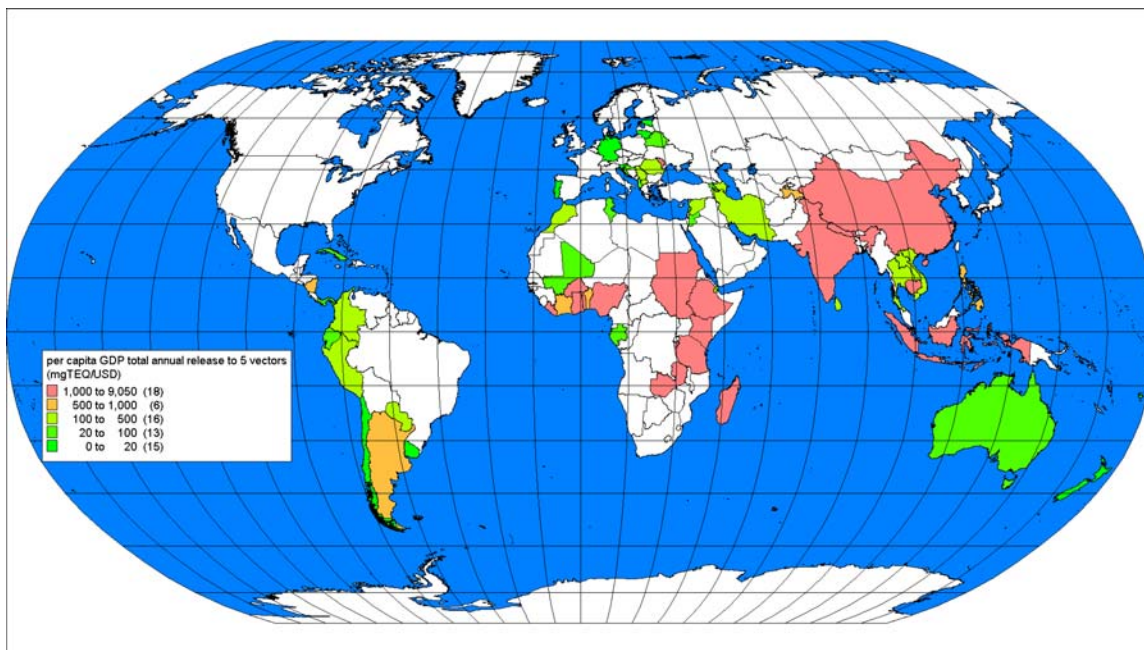


Figure III.7.10 Total annual releases according to per capita GDP (mg TEQ/USD person)



## Annex 8 Data quality

Because there is some level of uncertainty in all data, compiling inventories always entails uncertainty. There is uncertainty associated with data on both activity rates (*e.g.* reliability of data sources and data collection procedure) and emission factors (*e.g.* quality of measurement data). This is not a problem, since the purpose of the inventories is to assess the national situation by identifying sources and estimating releases of particular pollutants, setting priorities, developing an action plan to minimize these releases, and evaluating the progress achieved by assessing the trends observed over time. If the same methodology is consistently being applied when reassessing the country's situation regarding PCDD/PCDF emission, then this purpose can be met.

The following sources of uncertainty may be considered when developing a national PCDD/PCDF inventory:

**Default emission factors:** Two questions need to be answered when assessing emission factor quality:

- How reliable are the data that were used to derive the emission factor? and
- How well does the emission factor represent the emission source under different national circumstances, *i.e.* can it be appropriately used as a global average emission factor for a specific source activity?

Evaluation of the quality of emission factors included or to be included in the Toolkit is the mandate of the Toolkit experts, who should ascertain that only scientifically-sound data are included into the Toolkit. Data quality ratings are assigned by the Toolkit experts to all emission factors published in the Toolkit.

**Classifying sources:** There is uncertainty in classifying sources and, consequently, selecting appropriate emission factors from the Toolkit while developing the national inventory.

**Activity rates:** There is uncertainty in generating activity data for inventory compilation.

The overall level of uncertainty in the complete inventory is a combination of the above three elements.

The most complete guidance document currently available is the IPCC Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories. However, this document was developed with a different purpose, and is not suitable for developing PCDD/PCDF emission inventories under the Stockholm Convention.

For the purpose of emission inventories under the Stockholm Convention, a simple approach using qualitative data quality rating is recommended. An emission factor's rating is a general indication of the reliability, or robustness, of that factor. This rating is assigned based on the estimated reliability of the experiments used to develop the factor and on both the amount and the representative characteristics of those data. This approach can be used to assess the underlying confidence of the author of the inventory in the data used to generate emissions estimates. It is most suitable for estimation approaches that rely on emission factors, as well as estimates of activity rates. In all cases, higher quality ratings would be given to more direct approaches based on measurement data.

The following criteria are used to assign quality ranks to the Toolkit's emission factors:

- Data/information used to derive emission factors were evaluated by a formal process of peer review. Publications/reports, reviewed by the Toolkit expert group will equally be considered as peer-reviewed.
- Data range: High variability of available data may trigger the use of median emission factors that do not fully reflect certain operational circumstances. A wide range of the data used to derive an emission factor would therefore reduce the confidence in applying the respective emission factor to a concrete situation.
- Geographical coverage: Experimental data with low variability derived at many locations over the world would increase the confidence in using the respective emission factor in different national circumstances.
- Need for extrapolation: The need for extrapolation/expert judgment in order to fill data gaps reduces the confidence in the emission factors derived by making certain assumptions *e.g.* based on information from similar classes.
- Process stability: High stability of the process generating PCDD/PCDF generally increases the confidence in the experimental results used to derive emission factors. It should be noted that high variability of emission data may be obtained even with a stable process. High confidence levels are to be assigned to emission factors derived from data with well-described variability.

Taking into account the criteria described above, each emission factor is assigned a data quality rating according to the following definitions:

#### Rating of emission factors

Qualifier/Level of confidence	Criteria
<b>High</b>	Peer review Low data range Broad geographical coverage Assumptions and/or expert judgment are not required High stability of the process
<b>Medium</b>	Any combination of high and low criteria
<b>Low</b>	No peer review Wide data range Limited geographical coverage Extrapolation is needed <i>e.g.</i> EF derived from similar class Low stability of the process

The studies used to derive the Toolkit's emission factors are made accessible for the users whenever possible, to ensure that emission factors are applied with the specified level of confidence only when

they match a certain situation. Where expert judgment is used to derive emission factors, clear information on the extrapolation process is provided, along with justification of the assumptions made.

Ratings can be similarly assigned to the activity or production data, taking into account the reliability of the data source, data collection process, number of data points (*e.g.* for questionnaires) etc. According to these criteria, activity data taken from national statistics, or derived from questionnaires with a high return rate may be used with high confidence. Activity data based on assumptions about certain sources (especially with respect to technologies in place), where specific information could not be collected, will be assigned a low level of confidence.

Due to the iterative revision process of the Toolkit, the emission factors are periodically verified, updated and supplemented via targeted projects and research. Furthermore, as the focus of the Toolkit is exclusively on unintentional POPs, it can be regarded as a comprehensive compilation of emission factors for POPs releases to air, water, soil, products and residues.

## Annex 9 Complementary information to source category 1a Municipal Solid Waste Incineration

### Overview of recent revisions

No revisions were made to emission factors in this source category. Additional guidance has been introduced on classifying sources within this category, estimating activity rates, and on data quality aspects.

### Derivation of emission factors

#### Release to Air

For class 1, the default emission factor of 3,500 µg TEQ/t of waste burned was derived from a flue gas flow rate of about 10,000 Nm<sup>3</sup>/t MSW and a concentration of 350 ng TEQ/Nm<sup>3</sup> (at 11% O<sub>2</sub>). Emission factors of 3,230 µg TEQ/t have been reported from Switzerland and 5,000 µg TEQ/t from the Netherlands (LUA 1997).

For class 2, it is assumed that the specific flue gas volume is 7,000 Nm<sup>3</sup>/t MSW, due to better combustion controls and lower excess air and the PCDD/PCDF concentration is reduced to 50 ng TEQ/Nm<sup>3</sup> (at 11% O<sub>2</sub>). Plants of this type may be equipped with an ESP, multi-cyclone and/or a simple scrubber.

In class 3, the combustion efficiency and the efficiency of APC systems are further improved (*e.g.*, ESP and multiple scrubbers, spray-dryer and baghouse or similar combinations) so that the PCDD/PCDF concentration is reduced to about 5 ng TEQ/Nm<sup>3</sup> (at 11% O<sub>2</sub>). Also, the specific flue gas volume is reduced to 6,000 Nm<sup>3</sup>/t MSW.

Class 4 incinerators are the current state-of-the-art in MSW incineration and are equipped with advanced APC technology (*e.g.*, activated carbon adsorption units or SCR/DeDiox). Thus, only 5,000 Nm<sup>3</sup>/t MSW and a concentration of less than 0.1 ng TEQ/Nm<sup>3</sup> (at 11% O<sub>2</sub>) will be the norm (LUA 1997, IFEU 1998).

In a study of a Thai municipal solid waste incinerator, the flue gas concentrations at 11% O<sub>2</sub> ranged from 0.65 to 3.10 ng I- TEQ/Nm<sup>3</sup> with an average of 1.71 ng TEQ/Nm<sup>3</sup> (at 11% O<sub>2</sub>). The concentrations of total PCDD/PCDF (Cl<sub>4</sub>-Cl<sub>8</sub>) were between 41.3 and 239 with a mean of 122 ng/Nm<sup>3</sup> (at 11% O<sub>2</sub>) (UNEP 2001, Fiedler *et al.* 2002). The measured average concentration of 122 ng PCDD/PCDF/m<sup>3</sup> is above the Thai standard for municipal waste incinerators of 30 ng/m<sup>3</sup>; the mean of 1.7 ng TEQ/Nm<sup>3</sup> is also above the European standard of 0.1 ng TEQ/m<sup>3</sup>. The measured emissions would result in an emission factor of 6.1 µg TEQ/t of waste burned. The Toolkit would have classified this incinerator into class 3 and would have given an emission factor of 30 µg TEQ/t. By applying the Toolkit's default emission factor, the release would have been overestimated by a factor of 5 but would have fallen into the anticipated order of magnitude.

PCB emission factors to air have been determined in a measurement campaign in France (Delepine *et al.* 2011). For class 4, high technology MSW incinerators, emission factors in the range of 0.004 - 0.017 µg TEQ/ton of MSW incinerated are calculated for dioxin-like PCBs, and between 2 and 64 µg/t of MSW

incinerated for indicator PCBs.

### **Release to Water**

Releases to water may occur when wet scrubbers are employed for the removal of particulate matter or to cool down ashes. In such cases, the amount of PCDD/PCDF released through this vector, can best be estimated using the default emission factors given for residue. Normally, concentrations are in the range of a few pg TEQ/L and the highest PCDD/PCDF concentration reported in a scrubber effluent before removal of particulate matter was below 200 pg TEQ/L. Most of PCDD/PCDF are associated with the particulate matter and are consequently captured in the filter cake or sludge from treatment of the scrubber effluent. For inventorying purposes, these scrubber water treatment residues are included with fly ash.

### **Release to Land**

No release to land is expected unless untreated residue is directly placed onto or mixed with soil. The concentration released in such cases will be covered under "Release in Residues".

### **Release in Products**

The process has no product, thus there will be no emission factor.

### **Release in Residues**

PCDD/PCDF concentrations in fly ash are substantial, while the total mass generated per ton of MSW is typically around 4-9%. PCDD/PCDF concentrations in the bottom ash are rather low, however, the amount of bottom ash generated per ton of MSW is around 19-30% (UNEP 2011b). Fly ash and bottom ash also contain unburned carbon from 1% (class 4) up to 30% (class 1). Since unburned carbon in the ash greatly enhances the formation and adsorption of PCDD/PCDF, the concentration is greatest in class 1; here, 500 ng TEQ/kg was chosen for bottom ash. This value has been extrapolated; it is about 10-fold above the average measured concentrations from European plants in the 1980s.

In class 2 the concentration is assumed to be 30,000 ng TEQ/kg in fly ash and 100 ng TEQ/kg in bottom ash due to greatly improved combustion efficiency resulting in a much lower LOI of the ash.

For class 3, these values are assumed to be lower due to further improvements.

For class 4, high combustion efficiency, and very high collection efficiency, especially of the very small fly ash particles, are assumed. These small particles supply a large adsorption surface for PCDD/PCDF and therefore the overall concentration does not decrease further. Thus, the value for the fly ash is set at 1,000 ng TEQ/kg and the concentration for the bottom ash drops to 5 ng TEQ/kg.

## Annex 10 Complementary information to source category 1b Hazardous Waste Incineration

### Overview of recent revisions

No revisions were made to emission factors in this source category. Additional guidance has been introduced on classifying sources within this category, estimating activity rates, and on data quality aspects.

### Derivation of emission factors

Default emission factors are based on the assumption that the waste burned leads to about 3% of fly ash and the PCDD/PCDF release associated with the disposal of bottom ash is negligible in classes 3 and 4. No data exist for classes 1 and 2 for bottom ash concentrations. Also, the removal efficiency of particulate matter increases with the quality of the plant. Class 4 should only be used for highly sophisticated hazardous waste incineration plants in conjunction with a strictly enforced regulatory value of 0.1 ng TEQ/Nm<sup>3</sup> (at 11% O<sub>2</sub>), such as legislated in the European Union. The vast majority of all hazardous waste incineration plants can be assumed to fall into classes 2 and 3. Class 1 should be chosen mainly for very small (< 500 kg/h) and simple furnaces operated in a batch type mode without any APC system attached to the back end, *e.g.*, muffle ovens.

### Release to Air

The default emission factor for class 1 was derived from a specific flue gas volume flow rate of about 17,500 Nm<sup>3</sup>/t of hazardous waste and a concentration of about 2,000 ng TEQ/Nm<sup>3</sup>.

Class 2 assumes a reduction in the specific flue gas volume flow rate to 15,000 Nm<sup>3</sup>/t of hazardous waste due to better combustion controls and lower excess air. The PCDD/PCDF concentration drops to 20 ng TEQ/Nm<sup>3</sup> (at 11% O<sub>2</sub>) in this case.

In class 3, the combustion efficiency improves further and the efficiency of the APC system improves resulting in a drop of the PCDD/PCDF concentration to about 1 ng TEQ/Nm<sup>3</sup> (at 11% O<sub>2</sub>). Also, the specific flue gas volume flow rate is reduced to 10,000 Nm<sup>3</sup>/t HW.

Class 4 represents the current state-of-the-art in HW incineration and APC technology. Thus, only 7,500 Nm<sup>3</sup>/t HW and a concentration of significantly less than 0.1 ng TEQ/Nm<sup>3</sup> (at 11% O<sub>2</sub>) is realistic (LUA 1997, IFEU 1998, Environment Canada 1999).

PCB emission factors to air have been derived in a measurement campaign in France (Delepine *et al.* 2011). For class 4, high technology HW incinerators, emission factors in the range of 0.0004-0.237 µg TEQ/ton of HW incinerated are calculated for dioxin-like PCBs, and between 6–154 µg/t of HW incinerated for indicator PCBs.

### Release to Water

Releases to water occur when wet scrubbers are employed for the removal of particulate matter and when residue is cooled or washed with water. The amount of PCDD/PCDF released through this vector can best be estimated by using the default emission factors supplied for residue. The maximum actual

PCDD/PCDF concentration found in wet scrubber effluent was below 0.15 µg TEQ/t (LUA 1997). Overall, this release vector is not considered to be important for this source type.

### **Release to Land**

No release to land is expected unless untreated residue is directly placed onto or mixed with soil. The concentration released in such cases will be covered under "Release in Residues".

### **Release in Products**

The process has no product, thus no release to product occurs.

### **Release in Residues**

The amount of fly ash in hazardous waste is typically around 3%. Fly ash also contains unburned carbon of 0.5% (class 4) up to 20% (class 1). Since unburned carbon in the fly ash greatly enhances the adsorption of PCDD/PCDF, the concentration is greatest in class 1. In class 1, PCDD/PCDF was assumed to be around 300,000 ng TEQ/kg fly ash.

In class 2 the concentration drops to 30,000 ng TEQ/kg fly ash due to greatly improved combustion efficiency resulting in a much lower LOI of the fly ash.

Class 3 cuts this value down to 15,000 ng TEQ/kg fly ash based on further improvements.

Class 4 assumes not only high combustion efficiency but also very high collection efficiency, especially of the very small fly ash particles. Combined fly ash and boiler ash from a BAT-compliant hazardous waste incinerator has been determined to have a PCDD/PCDF concentration of 388.2 ng TEQ/kg and a generation rate of about 3 percent. With the inclusion of scrubber sludge, the PCDD/PCDF concentration decreased to 367.8 ng TEQ/kg at the same time the combined generation rate increased to 6.4% (van Caneghem *et al.* 2010). Bottom ash was generated at a rate of 24.6% and an emission factor of 10 ug TEQ/t waste was derived for bottom ash.

## Annex 11 Complementary information to source category 1c Medical Waste Incineration

### Overview of recent revisions

No revisions were made to emission factors in this source category. Additional guidance has been introduced on classifying sources within this category, estimating activity rates, and on data quality aspects.

### Derivation of emission factors

Default emission factors are based on the assumption that the medical waste burned leads to about 3% of fly ash and the PCDD/PCDF release associated with the disposal of bottom ash is uncertain. A bottom ash generation rate of ~10% has been reported (Alvim-Ferraz and Alfonso 2003, Grochowalski 1998) with an average concentration of 19.3 µg TEQ/kg (Grochowalski 1998). Also, the removal efficiency of particulate matter increases with the quality of the plant.

Class 1 should be chosen for very small and simple, small box type incinerators operated intermittently (in which a load of waste is ignited and left) with no secondary combustion chamber, no temperature controls and no pollution control equipment.

Class 2 applies to all medical waste incinerators with controlled combustion and equipped with an afterburner, which, however, are still operated in a batch type mode.

Class 3 should be applied for controlled batch-type plants, which have good APC systems in place, *e.g.*, ESPs or preferably baghouse filters.

Class 4 should only be used for highly sophisticated medical waste incineration plants, *e.g.*, if a limit value equivalent to 0.1 ng TEQ/Nm<sup>3</sup> (at 11% O<sub>2</sub>) is strictly enforced, and the facility can be assumed to be in compliance. In this latter case the question of continuous versus batch type operation will become irrelevant, since these facilities are usually preheated with oil or natural gas extensively. Only after the intended furnace operating temperature of usually well above 900°C is reached, medical waste is introduced into the furnace.

The vast majority of medical waste incineration plants can be assumed to fall into class 2. Larger, centralized plants may be grouped into class 3.

### Release to Air

The default emission factor for class 1 was derived from a specific flue gas volume flow rate of about 20,000 Nm<sup>3</sup>/t medical wastes burned and a concentration of about 2,000 ng TEQ/Nm<sup>3</sup> (at 11% O<sub>2</sub>).

Class 2 assumes a reduction in the specific flue gas volume flow rate to 15,000 Nm<sup>3</sup>/t medical wastes due to better combustion controls and lower excess air. The PCDD/PCDF concentration drops to 200 ng TEQ/Nm<sup>3</sup> (at 11% O<sub>2</sub>) in this case.

Class 3 is based on European data where a concentration of 35 ng TEQ/Nm<sup>3</sup> (at 11% O<sub>2</sub>) with 15,000 Nm<sup>3</sup>/t has been determined.



Class 4 represents the current state-of-the-art in medical waste incineration and good APC technology. In these cases, only 10,000 Nm<sup>3</sup>/t of medical waste was generated and a concentration of less than 0.1 ng TEQ/Nm<sup>3</sup> (at 11% O<sub>2</sub>) was measured (LUA 1997, IFEU 1998, Environment Canada 1999).

PCDD/PCDF concentrations emitted via the stack to air from a medical waste incinerator in Thailand – adjusted to 11% O<sub>2</sub> – were between 21.8 and 43 ng TEQ/Nm<sup>3</sup> for line A and between 10.7 and 45.0 ng TEQ/Nm<sup>3</sup> for line B; the averages were 33.8 and 28.6 ng TEQ/Nm<sup>3</sup>, respectively. These emissions resulted in an emission factor of approximately 1,200 µg TEQ/t of waste burned, which is between the class 2 (3,000 µg TEQ/t) and class 3 (525 µg TEQ/t) emission factors (UNEP 2001, Fiedler et al. 2002).

### **Release to Water**

Releases to water occur when wet scrubbers are employed for the removal of particulate matter and quench water is used to cool ashes. Measured concentrations of PCDD/PCDF in scrubber water after medical waste incinerators are not available. Where wet scrubbers and quenching of ashes are identified, the water treatment should be noted.

### **Release to Land**

No release to land is expected unless untreated residue is directly placed onto or mixed with soil. The concentration released in such cases will be covered under “Release in Residues”.

### **Release in Products**

The process has no product; thus no release to product occurs.

### **Release in Residues**

PCDD/PCDF concentrations in fly ash are substantial. Default emission factors provided in the residue category only relate to PCDD/PCDF releases via fly ash. A study of 18 medical waste incinerators reported PCDD/PCDF concentrations in bottom ash ranging from 8-45 µg TEQ/kg, with an average of 19.3 µg TEQ/kg (Grochowalski 1998). PCDD/PCDF concentrations in the residues can be especially high, when combustion is poor (*e.g.*, in a simple batch-type incinerator). Classes 1 and 2 medical waste incinerators will not generate fly ash due to the lack of dust removal equipment. In these cases, all residues will consist of the residue left in the combustion chamber. The class 1 emission factor is based on the assumption that the 200 kg of residue per ton of medical waste burned is left in the combustion chamber with a concentration of 1,000 ng TEQ/kg. For class 2, combustion is improved, so the bottom ash residue should contain only 100 ng TEQ/kg; resulting in an emission factor of 20 µg TEQ/t of waste.

For classes 3 and 4, the amount of fly ash typically is around 3%. Class 3 assumes 30,000 ng TEQ/kg in the fly ash and 100 ng TEQ/kg in the grate ash (same as class 2). Class 4 incinerators have high combustion efficiency, resulting in an organic carbon content of about 1% of unburned carbon but also a very high collection efficiency of the small fly ash particles. Fly ash is collected (30 kg/t of waste) with a concentration of 5,000 ng TEQ/kg fly ash and 10 ng TEQ/kg of grate ash is chosen. These small particles supply a large adsorption surface for PCDD/PCDF and therefore the overall concentration does not decrease any further.

The results from the medical waste incinerator in Thailand were extremely high due to the poor combustion conditions in the primary chamber and the operation on-site, where the bottom ashes were left overnight in the chamber to slowly cool down. Such conditions create high concentrations of PCDD/PCDF. We found bottom ash concentrations of 1,390 and 1,980 ng TEQ/kg of bottom ash, which is about 20 times higher than was expected for a class 2 bottom ash (UNEP 2001, Fiedler et al. 2002).

## **Annex 12 Complementary information to source category 1d Light Fraction Shredder Waste Incineration**

### **Overview of recent revisions**

No revisions were made to emission factors in this source category. Additional guidance has been introduced on classifying sources within this category, estimating activity rates, and on data quality aspects.

### **Derivation of emission factors**

The default emission factors are based on a fly ash generation rate of 3%. Class 1 includes very simple type combustors such as simple stationary grate furnaces with no combustion controls and no APC equipment attached. Batch type operated furnaces without any APC also fall into class 1.

Class 2 should be chosen for all other furnaces with some kind of combustion control technology such as under and/or over fire air, stoker controls, fluidized beds, etc. including the facilities with some kind of APC system such as an ESP, baghouse or wet scrubber for dust removal.

Class 2 also applies to LFSW incinerators with controlled combustion and adequate APC equipment, which, however, are still operated in a batch type mode. The vast majority of all LFSW incineration plants can be assumed to fall into classes 1 and 2.

Class 3 should only be used for highly sophisticated RDF incineration plants and only, if a regulatory value equivalent to 0.1 ng TEQ/Nm<sup>3</sup> (at 11% O<sub>2</sub>) is enforced, and the facility in question must be assumed to be in compliance.

### **Release to Air**

There are not many measured data from this type of activity. The default emission factor for class 1 was derived based on a emission factor of 1,000 ng TEQ/kg as determined by the US EPA during a barrel burn study of selected combustible household waste which closely resembles the composition of fluff.

Class 2 uses various emission data from a series of Western European and North American RDF facilities including Japanese fluidized bed combustors with minimal APC equipment. An emission factor of 50 µg TEQ/t was determined.

Class 3 represents the current state-of-the-art in LFSW incineration and APC technology. Thus, only 10,000 Nm<sup>3</sup>/t light-shredder waste and a concentration of less than 0.1 ng TEQ/Nm<sup>3</sup> (at 11% O<sub>2</sub>) is taken. In one study involving the combustion of shredder residue in an advanced incinerator, PCDD/PCDF concentrations in stack gas ranged from 4.93 to 14.82 pg TEQ/Nm<sup>3</sup> (11% O<sub>2</sub>) (Mancini 2010).

### **Release to Water**

Measured PCDD/PCDF concentrations found in scrubber effluent after LFSW incinerators are not available. No emission factor can be provided.

### **Release to Land**

No release to land is expected unless untreated residue is directly placed onto or mixed with soil. The concentration released in such cases will be covered under “Release in Residues”.

### **Release in Products**

The process has no product; thus no release to product occurs.

### **Release in Residues**

PCDD/PCDF concentrations in fly ash must be assumed to be high. The amount of fly ash in LFSW is typically around 3%. In class 1, no APC equipment is used and consequently no fly ash is collected but rather most of it is emitted to the atmosphere with the flue gas. Even though no specific collection device for fly ash is installed and the majority of the fly ash is discharged through the stack, some fly ash is expected to collect in the furnace and the ductwork leading to the stack as well as in the stack itself. Since unburned carbon in the fly ash greatly enhances the adsorption of PCDD/PCDF, the concentration is greatest in class 1. However, no accurate data is available for this class.

Class 3 assumes not only high combustion efficiency but also very high collection efficiency, especially for the very small fly ash particles. Thus, a value of 15,000 ng TEQ/kg ash is chosen. These small particles supply a large adsorption surface for PCDD/PCDF and therefore the overall concentration does not decrease any further (LUA 1997, IFEU 1998). In addition, PCDD/PCDF concentrations reported in fly ash are 98 ng TEQ/kg (boiler) and 27 ng TEQ/kg (bag filter) and 29 ng TEQ/kg in bottom ash (Mancini 2010).

## **Annex 13 Complementary information to source category 1e Sewage Sludge Incineration**

### **Overview of recent revisions**

No revisions were made to emission factors in this source category. Additional guidance has been introduced on classifying sources within this category, estimating activity rates, and on data quality aspects.

### **Derivation of emission factors**

#### **Release to Air**

Releases to air represent the most important vector for class 1 and class 2 sewage sludge incinerators. The default emission factor for class 1 was determined based on an average emission concentration of 4 ng TEQ/Nm<sup>3</sup> (at 11% O<sub>2</sub>) and a specific flue gas volume flow rate of about 12,500 Nm<sup>3</sup>/t of sewage sludge burned based on a Belgian study as well as value of 77 ng TEQ/kg reported from the UK for a multiple hearth furnace with ESP. For class 2, the emission factor is based on data from the Netherlands for fluidized bed plants with scrubbers and ESP. Class 3 is for fluidized bed plants with optimized air pollution control systems consistently meeting the emission limits equivalent to 0.1 ng TEQ/Nm<sup>3</sup> (at 11% O<sub>2</sub>) (from Canadian, German and Swiss measurements) (LUA 1997, IFEU 1998, Environment Canada 1999).

PCB emission factors to air have been derived in a measurement campaign in France (Delepine et al. 2011). For class 3, high technology sewage sludge incinerators, emission factors in the range of 0.001-0.004 µg TEQ/ton of sewage sludge are calculated for dioxin-like PCBs, and between 12 – 28 µg/t of sewage sludge incinerated for indicator PCBs.

#### **Release to Water**

PCDD/PCDF concentrations in scrubber effluent from sewage sludge incinerators are not available. However, when wastewater from wet scrubbers is treated and then reintroduced to the incinerator, no PCDD/PCDF are released from the incineration plant to water. Where plants use wet scrubbers or simple water quench is applied to cool down the off-gases or to quench grate ash this should be noted as well as the treatment and fate of the effluents. The European inventory reports concentrations between 1.2 and 6.5 pg TEQ/L in scrubber effluents from sewage sludge incinerators (EC 1999a).

#### **Release to Land**

No release to land is expected unless untreated residue is directly placed onto or mixed with soil.

#### **Release in Products**

The process has no product; thus no release to product occurs.

#### **Release in Residues**

UK testing of multiple hearth furnaces showed PCDD/PCDF in the grate ash at concentrations of 39 ng TEQ/kg and 470 ng TEQ/kg in fly ash from the ESP (Dyke et al. 1997). Rates of ash production were 430 kg per ton of grate ash and 13 kg per ton of ESP ash for the multiple hearth plant. Levels in ash (all the

ash was collected in the ESP) from fluidized bed combustion were much lower (<1 ng TEQ/kg). 373 kg of ESP ash was produced per ton of sludge combusted in the fluidized bed. Class 1 releases to residues (combined) are therefore 23 µg TEQ/ton of waste. Class 2 releases are 0.5 µg TEQ/ton of waste. Class 3 releases are estimated the same as class 2.

## **Annex 14 Complementary information to source category 1f Waste Wood and Waste Biomass Incineration**

### **Overview of recent revisions**

No revisions were made to emission factors in this source category. Additional guidance has been introduced on classifying sources within this category, estimating activity rates, and on data quality aspects.

### **Derivation of emission factors**

#### **Release to Air**

In modern facilities, biomass is burned in either stationary or circulating fluidized bed furnaces where the formation of PCDD/PCDF is limited due to good combustion conditions. Such plants would likely have effective pollution control systems, especially removal of particulate matter, which is critical for the operation of circulating fluidized bed furnaces. Other furnace types commonly used are vertical rotary stage or open hearth-type furnaces, grate-type furnaces or muffle-type furnaces.

The default emission factors for all three categories were determined based on reported emission concentrations between 130 µg TEQ/t (Belgian study) and 1 µg TEQ/t (Canadian and Swedish studies). Thus, for class 1 a default emission factor of 100 µg TEQ/t was chosen for those old uncontrolled facilities. Class 2 represents better controlled newer facilities. A default emission factor of 10 µg TEQ/t was assigned to this class. Finally, class 3 with a selected default emission factor of 1 µg TEQ/t includes all the modern facilities for waste wood and biomass combustion (LUA 1997, IFEU 1998, Environment Canada 1999).

#### **Release to Water**

PCDD/PCDF concentrations in scrubber effluent from waste wood and waste biomass incinerators are not available.

#### **Release to Land**

No release to land is expected unless untreated residue is directly placed onto or mixed with soil. The concentration released in such cases will be covered under "Release in Residues".

#### **Release in Products**

The process has no product; thus there will be no emission factor.

#### **Release in Residues**

PCDD/PCDF concentration in the ash will be high since the ash usually contains rather high concentrations of unburned carbon. Especially in older furnaces, higher gaseous emissions clearly indicate lower combustion efficiency resulting in higher concentrations of unburned carbon in the fly ash. Thus, high concentrations of PCDD/PCDF in the ash must be expected. Unfortunately, only very limited data from Canada as well as Germany was found indicating a wide range from as high as 23,000 ng TEQ/kg ash to as low as 3.7 ng TEQ/kg of ash. Based on the fact that the total ash concentration in waste wood and biomass averages between 3% and 10%, an average value of 5% was chosen. This leads

to a default emission factor of about 1,000 µg TEQ/t for class 1 and 0.2 µg TEQ/t for class 3. For class 2, a medium value was chosen due to lack of data (LUA 1997, IFEU 1998, Environment Canada 1999). In class 1, no APC equipment is used and consequently no fly ash is collected but rather most of it is emitted to the atmosphere with the flue gas. Even though no specific collection device for fly ash is installed and the majority of the fly ash is discharged through the stack, some fly ash is expected to be collected in the furnace and the ductwork leading to the stack as well as in the stack itself. Measured data for bottom ash could not be obtained, consequently the default emission factors for residue only consider fly ash.



## **Annex 15 Complementary information to source category 1g Destruction of Animal Carcasses**

### **Overview of recent revisions**

No revisions were made to emission factors in this source category. Additional guidance has been introduced on classifying sources within this category, estimating activity rates, and on data quality aspects.

### **Derivation of emission factors**

#### **Release to Air**

Release to air is the predominant vector for animal carcass burning. The default emission factors for all three classes were determined based on reported emission concentrations between almost 50 µg TEQ/100 kg body weight (UK study) and less than 0.5 µg TEQ/100 kg body weight (Austrian and German studies). Thus, for class 1 a default emission factor of 500 µg TEQ/t body weight was chosen for those old uncontrolled facilities as well as open burning of animal carcasses. Class 2 represents better-controlled newer facilities. A default emission factor of 5 µg TEQ/100 kg (= 50 µg TEQ/t) body weight was chosen based on data from Switzerland, Germany and the UK for this class. Finally, class 3 with a selected default emission factor of 5 µg TEQ/t body weight includes all the modern facilities for animal carcass combustion (LUA 1997, IFEU 1998).

#### **Release to Water**

PCDD/PCDF concentrations in scrubber effluent from animal carcass incinerators are not available

#### **Release to Land**

Release to land is only expected if the combustion of animal carcasses is performed directly on the ground.

#### **Release in Products**

The process has no product; thus no release to product occurs.

#### **Release in Residues**

PCDD/PCDF concentration in the ash is high since the ash usually contains rather high concentrations of unburned carbon. Especially in older furnaces and in open burning situations higher gaseous emissions clearly indicate lower combustion efficiency resulting in higher concentrations of unburned carbon in the fly ash. Thus, high concentrations of PCDD/PCDF in the ash must be expected. No data was found for assigning default emission factors.

## Annex 16 Complementary information to source category 2a Iron Ore Sintering

### Overview of recent revisions

A literature survey on source group 2 was conducted based on the information submitted by Toolkit expert panel members, and new data collected and assessed based on the examination of 71 reports and scientific articles. This survey resulted in the identification of possible new/revised emission factors for PCDD/PCDF and possible new emission factors for PCBs and HCB.

The assessment of recent scientific findings led to new proposals regarding emission factors for PCDD/PCDF releases, along with the revision of class definition and description. Changes to emission factors were made where significant differences were found between factors derived from recent scientific literature and those included in the Toolkit. In many instances, the literature review also enhanced the level of confidence associated with current dioxin emission factors.

The majority of PCDD/PCDF emission factors for source category 2a Iron Ore Sintering were confirmed; in the case of residues in classes 2 and 3, higher emission factors were proposed. New emission factors are also proposed for PCBs and HCB air emissions:

**Table III.16.1 PCB emission factors for source category 2a Iron Ore Sintering**

2a Iron Ore Sintering		Emission Factors ( $\mu\text{g TEQ/t sinter produced}$ )				
Classification		Air	Water	Land	Product	Residue
1	High waste recycling including oil contaminated materials, no or limited air pollution control	1				
2	Low waste use, well controlled plant	0.2				
3	High technology emission reduction	0.05				

**Table III.16.2 HCB emission factors for source category 2a Iron Ore Sintering**

2a Iron Ore Sintering		Emission Factors ( $\mu\text{g/t sinter produced}$ )				
Classification		Air	Water	Land	Product	Residue
1	High waste recycling including oil contaminated materials, no or limited air pollution control	1,000				
2	Low waste use, well controlled plant	1,000				
3	High technology emission reduction	300				

For PCB and HCB, default emission factors provided in the above tables are assigned:

- A medium level of confidence for class 2 (PCB) and class 3 (HCB), as emission factors are based on a low data range and not on expert judgment but are not derived from a broad geographical coverage;

- A low level of confidence for class 1 (PCB and HCB), class 2 (HCB) and class 3 (PCB), as emission factors are based on extrapolations and expert judgment.

## Derivation of emission factors

### Release to Air

Iron ore sinter plants have been identified as a major source of PCDD/PCDF to air in some countries. The highest emissions are expected from plants which have not made comprehensive attempts to reduce PCDD/PCDF emissions and use waste materials such as cutting oils, dust from the ESP, etc (class 1). The emission factor for this class – 20 µg TEQ/t – comes from two inventory studies using a gas volume of 2,000 Nm<sup>3</sup> per ton of sinter and a concentration of 10 ng TEQ/Nm<sup>3</sup> (HMIP 1995, SCEP 1994). At one plant in Germany, an emission factor of nearly 100 µg TEQ/t sinter has been determined; respective stack emissions were 43 ng TEQ/m<sup>3</sup> (LUA 1997). This emission factor was confirmed through the highest value observed in the European Union after the year 2000 which is 16 µg TEQ/t (BREF 2012).

For plants with low waste use, the class 2 emission factor is 5 µg TEQ/t based on studies from Belgium, Sweden, the Netherlands, and Germany (LUA 1997). This emission factor was confirmed by several publications. In the 2011 version of the iron and steel BREF (BREF 2012), the majority of values ranges from 2 to 6 µg TEQ/t (more than 12 plants). The CORINAIR database considers an emission factor of 1.8 µg TEQ/t where ESPs are used. Between 2002 and 2004, measurements have been achieved on three sinter plants using ESPs in the UK showing emission factors with a mean value of 2.2 µg TEQ/t (Aries *et al.* 2006).

For highest technology plants, where PCDD/PCDF emissions were addressed and major changes to technology and plant operation were realized, a class 3 emission factor of 0.3 µg TEQ/t is proposed. Improvements may include measures to reduce gas flows and multistage scrubbing with effluent treatment. The emission factor of 0.3 µg TEQ/t is based on a reduced gas flow of 1,500 Nm<sup>3</sup>/t and a concentration of 0.2 ng TEQ/Nm<sup>3</sup> (Smit *et al.* 1999, HMIP 1995). This emission factor is confirmed by the lowest emission factor (0.15 µg TEQ/t) observed in the European Union, during the data collection process which was achieved for the iron and steel BREF (BREF 2012). Data collected in Taiwan from 4 plants show emission factors ranging from 0.18 to 0.89 µg TEQ/t (Wang *et al.* 2009) whereas data collected in Japan provide a mean value of 0.27 µg TEQ/t (Iwata *et al.* 2008). Concentration measured in one Korean sinter plant was 0.45 ng TEQ/Nm<sup>3</sup> (Kim *et al.* 2005), which corresponds to an emission factor of 0.9 µg TEQ/t (assuming a gas flow of 2,000 Nm<sup>3</sup>/t of sinter). Where wet scrubbers are used in conjunction with an ESP, the mean PCDD/PCDF concentration from 9 measurements is 0.31 ng TEQ/Nm<sup>3</sup> (Guerriero *et al.* 2006), which, assuming a gas flow of 2,000 Nm<sup>3</sup>/t, corresponds to an emission factor of 0.62 µgTEQ/t.

Air emission data related to PCBs and HCB have also been identified in the literature. The European BREF document gives a PCB emission factor range of 0.025 to 0.18 µg TEQ/t (BREF 2012). Measurements carried out in Korea showed PCB concentrations of 0.018 ng TEQ/Nm<sup>3</sup> (Kim *et al.* 2005). Assuming a gas flow of 2000 Nm<sup>3</sup>/t, such concentration corresponds to an emission factor of 0.04 µg TEQ/t. Thirdly, measurements achieved in two Polish sinter plants gave similar results: 0.048 and 0.056 µg TEQ/t (Grochowalski *et al.* 2007). Hence, an emission factor of 0.05 µg TEQ/t is proposed for class 3 and an

emission factor of 0.2 µg TEQ/t for class 2. According to these references, the PCB share in the total TEQ is ranging from 4 to 9%. Therefore, an emission factor of 1 µg TEQ/t is proposed for class 1.

HCB data are provided by three references. Two Japanese studies have synthesized HCB measurement results and propose emission factors of 430 µg/t and 150 µg/t respectively (Ota *et al.* 2005, Sakai *et al.* 2009). Measurements were also carried out in Poland and HCB emission factors could be derived. Those are ranging from 640 to 1,730 µg/t (Grochowalski *et al.* 2007). Assuming that class 3 APC devices are the most efficient for HCB removal and that class 1 and 2 APC devices have similar removal efficiencies towards HCB emissions, an emission factor of 300 µg/t is proposed for class 3 and an emission factor of 1,000 µg/t for class 2 and class 1.

### **Release to Water**

A release to water may occur if there is a wet scrubber used in the process with an effluent discharge. No emission factor could be developed for this release route. Any liquid discharge should be noted, along with its quantity and any treatment.

### **Release to Land**

No release to land is expected. Dumping of residues to land should be noted.

### **Release in Products**

The product of this process is sinter, which is fed to the blast furnace. PCDD/PCDF present in the sinter will enter the blast furnace and are likely to be destroyed. Therefore no release in product can be assessed.

### **Release in Residues**

The main residue is expected to be in the form of dust collected in dust control devices. Some of it may be recycled to the process, or may be removed from the process as a waste. As de-dusting devices are more sophisticated in the case of classes 2 and 3, the corresponding emission factors should be higher than class 1.

Class 1 emission factor is derived from measurements carried out before 2005 when de-dusting systems were far from BAT. UK data on the amounts of PCDD/PCDF in dust from sinter plant ESPs give a range from 29 to 90 ng I-TEQ/kg. Only a small amount of sinter dust is disposed of (*e.g.*, in the UK, 700 t/a from a sinter production of 15.1 million tons of sinter – about 0.05 kg dust per ton of sinter). Data from Germany measured in 1993/94 were in the range of 196 to 488 ng I-TEQ/kg (EC 1999a). An emission factor of 0.003 is therefore proposed for class 1. The iron and steel BREF developed within the EU gives an emission factor range for residues ranging from 0.14 to 3.21 µg TEQ/t (BREF 2012). Besides, measurements carried out in Korea in 2008 gave emission factors ranging from 0.14 to 3.21 µg TEQ/t (Jin *et al.* 2009). These references lead to Toolkit emission factors of 1 and 2 µg TEQ/t for classes 2 and 3 respectively.

## Annex 17 Complementary information to source category 2b Coke Production

### Overview of recent revisions

New PCDD/PCDF data were found for coke production in class 2, with significant differences in values for air emissions, which are now considered more robust than those previously included in the Toolkit. Some new emission factors have also been developed with respect to PCBs and HCB air emissions:

**Table III.17.1 PCB emission factors for source category 2b Coke Production**

2b Coke Production		Emission Factors ( $\mu\text{g TEQ/t}$ coke produced)				
Classification		Air	Water	Land	Product	Residue
1	No gas cleaning	0.2				
2	APC with afterburner/dust removal	0.002				

**Table III.17.2 HCB emission factors for source category 2b Coke Production**

2b Coke Production		Emission Factors ( $\mu\text{g/t}$ coke produced)				
Classification		Air	Water	Land	Product	Residue
1	No gas cleaning					
2	APC with afterburner/dust removal	0.6				

These emission factors are provided with:

- A medium level of confidence for class 2, as emission factors are based on a low data range, they are not based on expert judgment, but are derived from a limited geographical coverage;
- A low level of confidence for class 1, as emission factors are based on extrapolation and expert judgment.

### Derivation of emission factors

#### Release to Air

Emissions to air can occur during charging and discharging of the coal/coke as well as during heating. As there is no gas conducted to a stack, the emission factors are hard to measure and are therefore subject to uncertainty. Emission factors from the 2005 version of the Toolkit were derived from a single publication which was released in 1994 (Bremmer *et al.* 1994). Two publications from 2009 helped reviewing those emission factors. These publications provide data from plants in Taiwan and China (Wang *et al.* 2009, Liu *et al.* 2009). Emission factors from plants which can be regarded as class 2 plants were assessed at 0.0134 and 0.024  $\mu\text{g TEQ/t}$  respectively. This assessment led to a revision of the emission factor for class 2 which is proposed to be set at 0.03  $\mu\text{g TEQ/t}$ . The original emission factor for class 1 is not changed, assuming 99% efficiency for class 2 APC devices.

A new emission factor for PCBs (class 2) is derived from measurements achieved in China (Liu *et al.* 2009). Assuming the same APC efficiency as for PCDD/PCDF removal, an emission factor for class 1 is proposed as well. The same publication concluded on an emission factor for HCB (0.6 µg/t). This emission factor is assigned to class 2 facilities.

### **Release to Water**

A release to water will occur if effluents from quenching or wet scrubbing are discharged. Two emission factors are given: 0.06 µg TEQ/t for untreated water and 0.006 µg TEQ/t for treated water (assumed to be 90% effective).

### **Release to Land**

No release to land is expected.

### **Release in Products**

Any PCDD/PCDF present in the coke product is expected to pass to other processes. No data were available to estimate these amounts.

### **Release in Residues**

Residues may arise from sludge in water treatment and from any collected solids. No data were available on PCDD/PCDF in the residues.

## Annex 18 Complementary information to source category 2c Iron and Steel Production and Foundries

### Overview of recent revisions

PCDD/PCDF emission factors for residues were revised for class 3 (iron and steel making). In particular, the previous definition of classes 2 and 3 (iron and steel making) only included clean scrap; this was revised to cover both clean and dirty scrap. As for iron foundries, the revised emission factors confirm in general the previous values. Regarding hot-dip galvanizing plants, air emission factors were confirmed while residues emission factors were significantly modified.

Emission factors for other unintentional POPs are listed below:

**Table III.18.1 PCB emission factors for source category 2c Iron and Steel Production and Foundries**

2c Iron and Steel Production and Foundries		Emission Factors (µg TEQ/t LS)				
Classification		Air	Water	Land	Product	Residue
<b>Iron and Steel Making</b>						
1	Dirty scrap (cutting oils, general contamination), scrap preheating, limited controls					
2	Clean scrap/virgin iron or dirty scrap, afterburner and fabric filter					
3	a. Clean scrap/virgin iron or dirty scrap, EAF equipped with APC designed for low PCDD/PCDF emission, b. BOF furnaces	<b>0.001</b>				
4	Blast furnaces with APCS	<b>0.001</b>				
<b>Iron foundries</b>						
1	Cold air cupola [or hot air cupola] or rotary drum with no gas cleaning					
2	Rotary Drum - fabric filter	<b>0.5</b>				
3	Cold air cupola – fabric filter [or wet scrubber]	<b>0.5</b>				<b>0.1</b>
4	Hot air cupola, or induction furnace – fabric filter	<b>0.02</b>				<b>0.01</b>

**Table III.18.2 HCB emission factors for source category 2c Iron and Steel Production and Foundries**

2c Iron and Steel Production and Foundries		Emission Factors (µg/t LS)				
Classification		Air	Water	Land	Product	Residue
<b>Iron and Steel Making</b>						
1	Dirty scrap (cutting oils, general contamination), scrap preheating, limited controls	<b>2500</b>				
2	Clean scrap/virgin iron or dirty scrap, afterburner and fabric filter	<b>2500</b>				

3	a. Clean scrap/virgin iron or dirty scrap, EAF equipped with APCS designed for low PCDD/PCDF emission, b. BOF furnaces	<b>2 BOF 2500 EAF</b>				
4	Blast furnaces with APCS	<b>1</b>				

For iron and steel making, emission factors for PCB/HCB are provided:

- With a medium level of confidence for HCB emissions related to classes 2 and 4, as emission factors are not based on expert judgment but are not derived from a broad geographical coverage;
- With a low level of confidence for HCB emissions related to classes 1 and 3 and for PCB emissions (all classes), as emission factors are based on extrapolations and expert judgment.

For iron foundries, emission factors for PCB are provided:

- With a medium level of confidence for class 3 and 4 air emissions and for class 4 residue releases, as emission factors are not based on expert judgment but are not derived from a broad geographical coverage;
- With a low level of confidence for class 2 air emissions and for class 3 residue releases, as emission factors are based on extrapolations and expert judgment.

## Derivation of emission factors

### Release to Air

#### I. Iron and steel making

PCDD/PCDF will be released into gases from furnaces. It can be difficult to capture all the gases from the process, and a large fraction of the gas and PCDD/PCDF may be present in fugitive emissions rather than in stack gases. Emissions seem to increase greatly by poor quality mixed scrap feeds, in particular where metal working residues, including cutting oils, are fed. The preheating of scrap to improve energy efficiency can lead to increased emissions as well; concentrations up to 9.2 ng TEQ/Nm<sup>3</sup> have been measured (Germany, LUA 1997). In Europe, PCDD/PCDF measurements gave emission factors that ranged 0.07-9 µg I-TEQ/t LS (liquid steel); based on European data, a conversion factor of 940 kg pig iron/t LS was used.

Regarding blast furnaces (class 4), flue gas volumes from hot stoves are between 100,000 and 600,000 Nm<sup>3</sup>/h per blast furnace. Emission factors determined from measurements from four EU member States were from <0.001 to 0.004 µg I-TEQ/t LS. Such data are confirmed by more recent measurements from the European Union, as the iron and steel BREF document reports an emission factor of 0.003 µg TEQ/t (BREF 2012).

In BOFs during oxygen blowing, converter gas is released, which contains small amounts of PCDD/PCDF. Basic oxygen steel making plants in Europe generally have quite low emission factors, slightly higher



than blast furnaces (with an upper end of 0.06 µg I-TEQ/t LS based on measured data). Polish data (Grochowalski *et al.* 2006) are consistent with this figure as an emission factor of 0.02 µg TEQ/t was derived from measurement at a plant scale. As emission factors of BOF are similar to those of class 3 EAF (see below), BOF are incorporated in class 3.

For electric arc furnaces, most measured emission data relate to plants using relatively clean scrap and virgin iron and which are fitted with some after-burners and fabric filters for gas cleaning. Emission factors derived from plants in Sweden, Germany, and Denmark gave emission factors between 0.07 and 9 µg I-TEQ/t LS. For the Toolkit, an emission factor of 3 µg TEQ/t LS is applied (class 2) (Bremmer *et al.* 1994, SCEP 1994, Napier 1998). This emission factor is supported by data from several publications issued between 2003 and 2009. For instance, the following emission factors were derived: 1.33-7.6 µg TEQ/t in Taiwan (Wang *et al.* 2009), 1.7 µg TEQ/t in Japan (Sakai *et al.* 2009), 4.8 µg TEQ/t in Italy (ENEA 2003).

Emissions from EAF plants using dirty scrap containing cutting oils or plastic materials as well as plants with scrap preheating and relatively poor controls were found to have higher concentrations of PCDD/PCDF in stack gases as found in Germany (SCEP 1994). In such cases, an emission factor of 10 µg TEQ/t LS is used (poor plants could emit more) for class 1. This emission factor is supported by data from many publications issued between 2004 and 2009. For instance, the following emission factors were derived: 6.3 µg TEQ/t in Taiwan (Hwang *et al.* 2006), 11-90 µg TEQ/t in Sweden (Oberg 2004).

Where careful controls are placed on the scrap used (excluding cutting oils and heavily contaminated scrap) and efficient gas cleaning is used with secondary combustion and fabric filters (sometimes in combination with a rapid water quench) emissions below 0.1 ng TEQ/Nm<sup>3</sup> can be achieved. For these plants an emission factor of 0.1 µg TEQ/t should be used (class 3). The same low concentrations were measured in the flue gases from basic oxygen furnaces; *e.g.* a median concentration of 0.028 ng I-TEQ/Nm<sup>3</sup> (LUA 1997). This emission factor is supported by data from many publications issued between 2003 and 2010. For instance, the following emission factors were derived: 0.3-0.92 µg TEQ/t in New Zealand (Merz 2004, Graham and Bingham 2010), 0.03 µg TEQ/t in Sweden (Oberg 2004), 0.26 µg TEQ/t in Italy (ENEA 2003).

Regarding PCBs, based on results got on industrial sites from Poland (Grochowalski *et al.* 2006), an emission factor of 0.001 µg TEQ/t is proposed for classes 3 and 4.

Regarding HCB, Japan measurements on EAFs have been published for the last years in several publications (Ota *et al.* 2005, Sakai *et al.* 2009). EAF emission factors range between 2,100 and 2,900 µg/t. As a consequence, the same emission factor is proposed for EAFs related to classes 1 to 3. Measurements at a BOF and a blast furnace in Poland correspond to an emission factor of 2 µg/t and 1 µg/t respectively (Grochowalski *et al.* 2006).

## **II. Iron foundries**

For foundries, there are hardly any data available: testing in Germany (SCEP 1994) showed that hot air cupolas and induction furnaces fitted with fabric filters had low emissions to air, an emission factor of 0.03 µg TEQ/t of product should be used (class 4). This initial emission factor has been confirmed by

recent measurements carried out in France (0.0087 µg TEQ/t, Duquet and Fiani 2006), in Poland (0.02-0.06 µg TEQ/t, Grochowalski *et al.* 2006) and in South Korea (0.1 µg TEQ/t, Yu *et al.* 2006).

Cold air cupolas showed higher emissions and a factor of 1 µg TEQ/t is used for plants with fabric filters, (class 3). This initial emission factor has been confirmed by recent Chinese measurements (Lv *et al.* 2011a).

Limited testing on rotary drum furnaces showed higher levels again and a factor of 4.3 µg TEQ/t is applied to plants with fabric filters for gas cleaning (class 2).

Where cold air cupolas or rotary drum furnaces are used which do not have fabric filters or equivalent for gas cleaning a higher emission factor of 10 µg TEQ/t should be used (class 1).

If poor quality scrap (high contamination) or poorly controlled furnaces with gas cleaning other than effective fabric filters is found this should be noted.

Regarding PCBs, new data have been published since 2005. A Chinese team (Lv *et al.* 2011a) reported an emission factor of 0.5 µg TEQ/t for cold air cupolas (class 3) while a South Korean team (Yu *et al.* 2006) reported an emission factor range of 0.01-0.03 µg TEQ/t for hot air cupolas (class 4). As class 2 and 3 emission factors for PCDD/PCDFs are very similar, it is proposed to use the same PCB emission factor for these two classes.

### **III. Hot-dip galvanizing plants**

For hot-dip galvanizing plants, as for any other thermal plant, the presence or absence of flue gas cleaning equipment, will be a determining factor as to the magnitude of the PCDD/PCDF air emissions. Some plants do not have flue gas cleaning devices, others have bagfilters. From Germany and without further specification, PCDD/PCDF concentrations between 0.007 and 0.132 ng I-TEQ/Nm<sup>3</sup> were measured in the flue gases from four installations (LUA 1997); the median was 0.016 ng I-TEQ/Nm<sup>3</sup>. The Danish inventory utilized the German data and a stack volume of 33,000 Nm<sup>3</sup> emitted per ton of iron/steel galvanized to estimate its national emissions.

A Spanish study (Fabrellas *et al.* 2003), investigated hot-dip galvanizing plants equipped with bagfilters. The concentrations – 0.003-0.014 ng I-TEQ/Nm<sup>3</sup> - were much lower than those reported by Germany (LUA 1997). Nevertheless, the emission factor to air reported in these two studies were very similar: Spanish study =0.041-0.061 µg I-TEQ/t of galvanized steel and 0.007-0.027 µg I-TEQ/t of galvanized steel for plants without and with degreasing step, respectively; whereas the German study resulted in an air emission factor of 0.061 ng I-TEQ/t of galvanized steel. The Spanish team has carried out further measurements on six plants (Martinez *et al.* 2008): emission factors ranging from 0.007 to 0.061 were derived.

### **Release to Water**

Releases to water could occur where wet scrubbers or quenches are used. No data were available to provide an emission factor. Where an effluent is released this should be noted and information reported.

### **Release to Land**

No release to land is expected.

### Release in Products

No significant release is expected with the product steel from this process, it has been subject to high temperatures and PCDD/PCDF is likely to have been driven off or destroyed.

### Release in Residues

The principal residues of interest are slag and dust collected in flue gas treatment systems. Other dust deposited from fugitive emissions may also contain PCDD/PCDF.

#### I. Iron and steel making

From blast furnaces, 9-15 kg of dust and sludge per ton of LS are generated from the gas purification system. 280 kg of slag are produced per ton of LS.

In BOF steel making, 12-27 kg of dusts and slags are generated per ton of LS from BOF gas treatment. Converter slag is 99 kg per ton of LS. Electric arc furnaces produce more slags, e.g. 129 kg/t LS for carbon steels and 161 kg/t LS for high alloyed and stainless steels.

An average emission factor for PCDD/PCDF in residues can only be given for EAFs: from gas cleaning operations (fabric filter) an emission factor of 15 µg TEQ/t is based on an average of UK data (Dyke *et al.* 1997). This factor assumes similar gas cleaning equipment; the release may be different with other systems. This factor is used for the poorly controlled and average plants (classes 1 and 2). Such emission factor has been confirmed by recent publications. The following emission factors have been derived recently: 22 µg TEQ/t (Chang *et al.* 2006), 32 µg TEQ/t (Du *et al.* 2009).

A lower emission factor of 0.15 µg TEQ/t is used for the best plants (Bremmer *et al.* 1994): class 3. The fate or use of the residues should be noted (PCDD/PCDF can be introduced into other processes if these residues are used as feedstock in recycling processes).

#### II. Iron foundries

From foundries, cupolas and EAFs emit particulate matter, which is likely to contain PCDD/PCDF. Induction furnaces emit much less particulates. Initial emission factors were derived from data obtained in Germany (SCEP 1994). Slag can be generated as well as sand casting technologies will generate substantial volumes of sand, which may be reused in the plant or be sent off for use as construction material (USEPA 1998b). These emission factors have been confirmed by some recently published data from other parts of the world. For instance, measurements carried out in 14 Chinese foundries which can be allocated to classes 3 and 4 showed an average emission factor of 0.365 µg TEQ/t.

First PCB data with respect to residues were published recently (Lv *et al.* 2011a). From these results, emission factors of 0.1 µg TEQ/t and 0.01 µg TEQ/t are proposed for classes 3 and 4 respectively.

#### III. Hot-dip galvanizing plants

PCDD/PCDF concentrations in fly ashes from hot-dip galvanizing plants were measured to be 2.15-9.6 ng I-TEQ/kg ash with a geometric mean of 3.9 ng I-TEQ/kg fly ash (German data in LUA 1997); no emission factor can be derived from these data. The Spanish study did derive emission factor ranges of 487-8,075

pg I-TEQ/g of filter dust for plants without degreasing step and of 127-1,804 pg I-TEQ/g of filter dust for plants with degreasing step, respectively (Fabrellas *et al.* 2003). The mean value for both cases is 2,000 pg TEQ/g of filter dust. Based on Spanish and Danish publications (Martinez *et al.* 2008, Hansen 2001), it is assumed that 1 kg of filter dust is generated by the air pollution control for each ton of galvanized steel produced. As a consequence and assuming that higher emission factors are expected in the case of facilities without degreasing step, emission factors for classes 2 and 3 are proposed to be set at 2 µg TEQ/t and 1 µg TEQ/t respectively.

With respect to class 1, emission factors are based on ash residues concentrations measured in Spain (Martinez *et al.* 2008) and in China (Lv *et al.* 2011b). The Spanish team measured concentrations of 0.7-107 pg TEQ/g of ashes (n = 9), giving a mean value of 20 pg TEQ/g of ashes. The Chinese team obtained a similar result (12-38 pg TEQ/g of ashes). From this figure, the Chinese team derived an emission factor of 0.00065-0.0167 µg TEQ/t of galvanized steel. Therefore an emission factor of 0.01 µg TEQ/t galvanized steel is proposed for class 1.

## Annex 19 Complementary information to source category 2d Copper Production

### Overview of recent revisions

PCDD/PCDF emission factors are generally confirmed for source category 2d. No data could be found on class 6 (pure primary Cu smelters with no secondary feed materials). New data have been found on PCDD/PCDF releases through the water vector as well as on PCBs.

**Tabl1 III.19.1 PCB emission factors for source category 2d Copper Production**

2d Copper Production		Emission Factors (µg TEQ/t copper)				
		Air	Water	Land	Product	Residue
1	Sec. Cu – Basic Technology					
2	Sec. Cu – Well controlled	5				40
3	Sec. Cu –Optimized for PCDD/PCDF control	0.3				
4	Smelting and casting of Cu/Cu alloys					
5	Prim. Cu, well-controlled, with some secondary feed materials	0.01				
6	Pure primary Cu smelter with no secondary feed materials					

PCB emission factors are provided with:

- A medium level of confidence for class 2 and 5 air emissions, as emission factors are not based on expert judgment but are not derived from a broad geographical coverage;
- With a low level of confidence for class 3 air emissions and class 2 residue releases, as emission factors are based on extrapolations and expert judgment.

### Derivation of emission factors

#### Release to Air

Emissions to air from copper production seem to vary considerably depending on the process technology, the nature of the materials processed and the gas cleaning system applied. The occurrence of PCDD/PCDF is principally associated with secondary copper production.

The following data are from secondary copper facilities. A study in the US on a copper production plant using a blast furnace and fitted with afterburners and fabric filters, gave an emission factor of 779 µg TEQ/t of scrap.

Studies in Germany on several plants gave emission concentrations, which varied over a large range from 0.032 to 30 ng TEQ/Nm<sup>3</sup> (LUA 1997). Installations for smelting and casting of copper and its alloys, e.g. brass, gave emissions between 0.003 and 1.22 ng I-TEQ/Nm<sup>3</sup> with a geometric mean of 0.11 ng

TEQ/Nm<sup>3</sup> (German data, LUA 1997). The compilation for European plants by the IPPC Bureau reported emissions of <0.1 ng I-TEQ/Nm<sup>3</sup> (BREF 2009). From these data, an emission factor of 0.03 µg TEQ/t of copper/copper alloy was derived. The data do not allow for further differentiation according to technology or performance.

In the cleaned gases from sulfuric acid plants, emissions between 0.01 and 0.001 ng TEQ/Nm<sup>3</sup> have been measured (BREF 2009). The same sources report – without further specification - that processes in the melt shop for the production of semis (semi-manufactures such as alloy cast ingots, foils, sheet, strip) gave emission factors for electric furnaces of <5 µg and for shaft and rotary furnaces of <10 µg TEQ/t, respectively.

Measured PCDD/PCDF results are available from Germany (Meyer-Wulf 1996) and Sweden (LUA 1997). However, it should be noted that these plants as well as those in Canada are not “pure” primary copper smelters since they process significant amounts of recyclable materials (Copper Smelters 2004). Measured data from Germany from such a “primary” copper smelter, that uses considerable amounts of secondary materials as feed (up to 40%) in flash smelting furnaces and matte converters gave emissions between 0.0001 and 0.007 ng TEQ/Nm<sup>3</sup> resulting in a very narrow range of emission factors from 0.002 and 0.02 µg TEQ/t of copper (LUA 1997). Meyer-Wulf (1996) reported raw gas concentrations after the primary smelter between 0.004 ng I-TEQ/Nm<sup>3</sup> and 0.3 ng I-TEQ/Nm<sup>3</sup> whereas the higher concentrations were obtained when PVC was present in the recycled materials. Purified gases after the H<sub>2</sub>SO<sub>4</sub> plant were either non-quantifiable or 0.001 ng I-TEQ/Nm<sup>3</sup>. The EU Dioxin Inventory report of 1997 (LUA 1997) reports concentrations of 0.005-0.015 ng I-TEQ/m<sup>3</sup> in the waste gases from the roasting furnace for ore desulphurization. The volume of the waste gas was 5,000 Nm<sup>3</sup> per ton of copper produced. In addition, from a Swedish primary smelter that recycles considerable amounts of secondary materials, which produced 2,000 Nm<sup>3</sup>/t of waste gases, a concentration of 11 ng I-TEQ/m<sup>3</sup> was reported. From the results of the measurements given above, emission factors between 0.25 µg I-TEQ/t (from German results) and 22 µg I-TEQ/t (from Swedish results) were derived. The Belgium inventory took an emission factor of 10 µg I-TEQ/t to estimate its national releases (LUA 1997). The data in the upper range reflect more classes 2 and 3.

Globally speaking, the assessment made for the 2005 version of the Toolkit was confirmed by the literature review conducted between 2007 and 2012:

- Class 1: Concentrations of 63, 199 and 246 ng TEQ/Nm<sup>3</sup> were measured at the outlet of a furnace (before a bag filter) in Chinese plants (Hung *et al.* 2009). These concentrations corresponds to emission factors of 328, 1037 and 1282 µg TEQ/t respectively, based on gas flows used in another Chinese publication (Ba *et al.* 2009). In the draft revised BREF on the non-ferrous metal industry (BREF 2009), the highest European concentrations reported in installations where no APC was used reached 29.5 ng TEQ/Nm<sup>3</sup>. Assuming a gas flow of 10,000 Nm<sup>3</sup>/t, such a concentration corresponds to an emission factor of 295 µg TEQ/t.
- Class 2: Data obtained in China (Ba *et al.* 2009) and Taiwan (Yu *et al.* 2006) are very similar. The former publication provides an emission factor of 14.8 µg TEQ/t and the latter provides an emission factor of 24.5 µg TEQ/t.

- Class 3: Data collected on a Chinese plant using a bag filter and activated carbon injection show that PCDD/PCDF concentrations can reach 0.1-0.7 ng TEQ/Nm<sup>3</sup>, corresponding to an emission factor range of 0.5-3.65 µg TEQ/t (Hung *et al.* 2009). In Korea, concentrations of 0.63 ng TEQ/Nm<sup>3</sup> were measured (Kim *et al.* 2005), resulting in an emission factor of 6.3 µg TEQ/t, based on the assumption that the gas flow is 10,000 Nm<sup>3</sup>/t.
- Class 5: Three publications directly provide emission factors (Iwata *et al.* 2008, Grochowalski *et al.* 2007, Yu *et al.* 2006): 0.43, 0.04 and 0.014 µg TEQ/t respectively. These data were collected from plants located in Japan, Poland and Korea.

So far, there only are few data on releases of PCDD/PCDF from class 6 copper plants. The majority of information is from secondary copper plants, where occasionally high PCDD/PCDF emissions were found in the stack gases. When compiling this Toolkit, no measured data of PCDD/PCDF emissions or releases from pure primary copper smelters have been submitted nor found elsewhere. In some countries, like Chile, among others, primary copper smelters use only ores and concentrates and do not mix with secondary materials. In other countries, like Germany, Sweden, and Canada, among others, primary copper smelters receive feeds that include scrap and other recycled materials that are introduced in these “primary” copper smelters at rates between 15% and 40% (COCHILCO 2004). For the pure primary copper smelters as present, among others, in the Chilean copper foundries, the probability to form PCDD/PCDF in the production of primary copper seems to be very low or not existing. These primary foundries use clean raw materials and use either the base smelting process (with furnaces like the Teniente or the Noranda) or the flash smelting (with Outokumpu furnace). The white copper or concentrates from the furnaces are converted into copper blister in an oxygen-rich atmosphere by utilizing the Peirce-Smith Converter. Typical temperatures in the smelting processes are well above the critical temperatures reported for PCDD/PCDF formation: in the Teniente, the gases are at 1,260°C in a sulphur dioxide-rich atmosphere (at 25%), the liquid white copper at 1,240°C, and the liquid slags the temperature is 1,240°C. In the Outokumpu flash furnace the temperature is around 1,260°C and the gases leave at 1,300°C-1,350°C. The Pierce-Smith Converter operates in a temperature range of 1,150°C-1,250°C. The refining of the copper blister – to remove sulphur and oxygen - takes place in rotary kilns at an operational temperature around 1,200°C. The slags still have quite high copper contents (4%-10%) and are treated in the Teniente furnace, electric arc furnaces, or slag flotation plants at temperatures above 1,200°C. Purification of gases originating from the smelting furnaces and the converters is done by rapid quench, followed by electrostatic precipitators and washing towers and wet scrubbers. The sulphuric acid plants (H<sub>2</sub>SO<sub>4</sub> plants) apply catalytic converters (COCHILCO 2004).

New data have been identified with respect to PCB air emissions. PCBs were measured at the stack of a primary copper plant corresponding to class 5 (Yu *et al.* 2006). On this Korean plant, a concentration of 0.08 ng TEQ/Nm<sup>3</sup> was measured, from which an emission factor of 0.012 µg TEQ/t was derived by the authors. PCBs were also measured on three primary smelters in Poland, where concentrations were in the range of 0.0004-0.0035 ng/Nm<sup>3</sup>. Based on PCDD/PCDF data, these concentrations would correspond to a PCB emission factor of 0.001 µg TEQ/t. Therefore, an emission factor of 0.01 µg TEQ/t is proposed for class 5. Regarding class 3, concentrations measured in Belgium and in Korea are similar, as those are ranging from 0.026 to 0.046 ng TEQ/Nm<sup>3</sup> (Kim *et al.* 2005, François *et al.* 2005). Assuming a gas flow of

10,000 Nm<sup>3</sup>/t, these concentrations correspond to an emission factor of 0.3 µg TEQ/t on average. In two references, emission factors to be assigned to class 2 are calculated: 0.098 and 9.8 ng TEQ/t respectively (Ba 2009, Yu 2006). Therefore a PCB emission factor of 5 µg TEQ/t is proposed for class 2.

New data have also been identified regarding HCB air emissions from primary copper production (Iwata 2008). This Japanese publication proposed an emission factor of 11,000 µg/t. This figure is assigned to class 5.

### **Release to Water**

These may occur if effluents are discharged and the concentration is likely to be influenced by any water treatment applied. Any liquid release should be noted along with its source and treatment applied.

One set of data is available from a Swedish plant which is one of the largest copper smelter of its kind worldwide (Jansson *et al.* 2009). This plant processes ores and secondary raw material such as electronic scrap. Three different effluents were sampled and analyzed, with two replicate samples collected for each effluent. The effluent consisting of purified process water and water used in the production of sulfur dioxide, mixed with cooling water showed concentrations of 3.7 to 9.1 ng TEQ/Nm<sup>3</sup>. Taking into account the effluent flow on this site, this range corresponds to an emission factor range of 0.2-0.5 µg TEQ/t. The two other flows consist of cooling water, where emission factors are lower (1 to 20 ng TEQ/t). As this Swedish site processes a large range of feed materials, a common emission factor of 0.5 µg TEQ/t is proposed for all classes under category 2d.

### **Release to Land**

No release to land is expected.

### **Release in Products**

No releases to with the products are expected.

### **Release in Residues**

PCDD/PCDF will be found in the solid residues from the process. The principal concern is the residues from the gas treatment equipment. Dusts and sludge collected from gas treatment may be highly enriched in PCDD/PCDF. Concentrations of up to 20,000 ng TEQ/kg have been reported (SCEP 1994).

UK data (Dyke *et al.* 1997) suggests approximately 2,000 t of filter dusts arise from production of 46,000 t of copper. Combined with an average concentration of 14,400 ng TEQ/kg in the dust (SCEP 1994) this resulted in the 2005 Toolkit emission factor of 630 µg TEQ/t of product. This estimate, which was originally considered highly uncertain, has been confirmed by subsequent references from China and Korea (Ba *et al.* 2009, Yu *et al.* 2006).

For high technology plants a lower emission factor of 300 µg TEQ/t was originally proposed in the 2005 Toolkit. This rough estimate has been confirmed by subsequent references. For instance, an emission factor of 116 µg TEQ/t was assessed from Korean data (Jin *et al.* 2009).

For class 2, a PCB emission factor of 40 µg TEQ/t is proposed from two references where 4.17 µg TEQ/kg of residues and 0.13 µg TEQ/kg of residues are reported (Ba *et al.* 2009, Yu *et al.* 2006).



It should be noted that solid residues from the copper smelters may be recycled internally or be transferred to other secondary metal reclamation plants. In such cases, the solid residues constitute an intermediate and its PCDD/PCDF release will not be taken into account in the national PCDD/PCDF release inventory.

## Annex 20 Complementary information to source category 2e Aluminum Production

### Overview of recent revisions

New data confirmed the majority of PCDD/PCDF emission factors for this source category, with slightly higher values for residues (class 3). New emission factors are proposed for HCB and PCBs.

**Table III.20.1 PCB emission factors for source category 2e Aluminum Production**

2e Aluminum Production		Emission Factors ( $\mu\text{g TEQ/t aluminum}$ )				
Classification		Air	Water	Land	Product	Residue
1	Thermal processing of scrap Al, minimal treatment of inputs and simple dust removal	40				
2	Thermal Al processing, scrap pre-treatment, well-controlled, fabric filters with lime injection	0.1				20
3	Optimized for PCDD/PCDF control – afterburners, lime injection, fabric filters and active carbon	0.02				
4	Shavings/turning drying (simple plants)					
5	Thermal de-oiling of turnings, rotary furnaces, afterburners, and fabric filters					
6	Primary Al production					

**Table III.20.2 HCB emission factors for source category 2e Aluminum Production**

2e Aluminum Production		Emission Factors ( $\mu\text{g/t aluminum}$ )				
Classification		Air	Water	Land	Product	Residue
1	Thermal processing of scrap Al, minimal treatment of inputs and simple dust removal	500				
2	Thermal Al processing, scrap pre-treatment, well-controlled, fabric filters with lime injection	500				
3	Optimized for PCDD/PCDF control – afterburners, lime injection, fabric filters and active carbon	500				
4	Shavings/turning drying (simple plants)					
5	Thermal de-oiling of turnings, rotary furnaces, afterburners, and fabric filters					
6	Primary Al production					

Emission factors for PCB/HCB are provided with:

- A high level of confidence for class 2 air emissions (PCB), as emission factors are derived from a broad geographical coverage and are based on a low data range and not on expert judgment;

- A medium level of confidence for class 2 air emissions (HCB), as emission factors are not based on expert judgment but are not derived from a broad geographical coverage;
- A low level of confidence for all other classes (PCB/HCB), as emission factors are based on extrapolations and expert judgment.

## Derivation of emission factors

### Release to Air

Several steps in the processing of aluminum scrap can lead to the release of PCDD/PCDF to air. Thermal pretreatment of input materials, scrap melting and metal refining using chlorine or hexachloroethane (as a degasifying agent) can all lead to releases of PCDD/PCDF to air.

Emissions to air vary greatly depending on the nature of the scrap, pre-cleaning of the feed and the type of furnace and gas cleaning system applied. Older technology furnaces fitted with fabric filters had emissions of 146 to 233 µg TEQ/t of product. Concentrations and volumes of flue gas vary considerably; concentrations up to 10 ng I-TEQ/m<sup>3</sup> were reported (SCEP 1994). Drum furnaces using aluminum turnings seemed to produce high emissions. For systems using contaminated scrap (such as scrap with cutting oils, plastics) with simple controls and gas cleaning consisting of cyclones or basic fabric filters an emission factor of 100 µg TEQ/t of product should be used.

The class 2 emission factor of 3.5 µg TEQ/t is taken from recent measurements at two European plants and are for well-controlled modern plants with scrap treatment, fabric filters, and lime injection. The Italian study gave 5.2 µg TEQ/t of Al. Class 2 emission factor was confirmed by a number of publications released between 2005 and 2010. Emission factors of 0.3 to 8.6 µg TEQ/t were derived in Poland (Grochowalski *et al.* 2007), 2.9 µg TEQ/t in New Zealand (Graham and Bingham 2010), 7-8 µg TEQ/t in Japan (Iwata *et al.* 2008), 1.24 µg TEQ/t in South Korea (Yu *et al.* 2006), 2.65 µg TEQ/t in China (Ba *et al.* 2009).

Class 3 emission factor should be applied for plants equipped with dioxin reducing technology, especially optimized flue gas cleaning systems. Class 4 emission factors are confirmed by measurements carried out on industrial plants in New Zealand (Merz 2004) and in Italy (Pitea *et al.* 2008). In New Zealand, emission factors ranging from 0.0027 to 0.5 µg TEQ/t were calculated. In Italy, an emission factor of 0.35 µg TEQ/t was derived from various measurements on a plant optimized for PCDD/PCDF controls. In Taiwan, PCDD/PCDF emissions from secondary smelters fed with aluminum ingots and very clean scrap were in the range of 0.025-0.441 µg TEQ/t, bringing additional confirmation for class 4 emission factor.

Classes 4 and 5 emission factors address plants for de-oiling and drying of Al turnings: class 4 emission factor of 5 µg TEQ/t applies to the drying of Al shavings and turnings in rotary drums or similar equipment and class 5 emission factor applied to thermal de-oiling of turnings in rotary kilns with afterburners and fabric filters (ENEA 2003).

Regarding PCB emissions, from measurements carried out in Poland (Grochowalski *et al.* 2007), in China (Ba *et al.* 2009) and in South Korea (Yu *et al.* 2006) on plants assigned to class 2, emission factors ranging from 0.04 to 0.81 µg TEQ/t were derived. Thus, an emission factor of 0.1 µg TEQ/t is proposed for class 3. Emission factors for class 1 are based on Japanese data (Takeuchi *et al.* 2009) and Spain (Sanz *et al.*

2010) where respective concentrations of 7 and 3 ng TEQ/Nm<sup>3</sup> are reported, which correspond to an average emission factor of 40 µg TEQ/t. Class 3 PCB emission factor is estimated from class 2 PCB emission factor and class 3 and class 2 PCDD/PCDF emission factors.

Regarding HCB emissions, data reported in the literature and derived from Japanese plants assigned to classes 1, 2 and 3 were very similar. Class 3 emission factors were in the range of 23-7,200 µg/t (Iwata *et al.* 2008). Class 2 emission factors assessed were in the range of 23-3,600 µg/t (Ota 2005). Class 1 emission factors assessed were in the range 450-1,300 µg/t (Takeuchi *et al.* 2009). Therefore, the same emission factor is proposed for classes 1 to 4 (500 µg/t).

### **Release to Water**

Releases to water may result where wet scrubbers or other processes have liquid effluents. There is insufficient information to estimate emission factors. Any liquid effluents should be noted and their source recorded.

### **Release to Land**

No release to land is expected.

### **Release in Products**

No releases into the products are expected.

### **Release in Residues**

Residues from the process are expected to contain PCDD/PCDF. The highest contamination is expected to be associated in dust and sludge from flue gas treatment. The amounts of such dust and sludge should be recorded and any use in other processes may lead to transfer of PCDD/PCDF. Melting in rotary drum furnaces generates 300-500 kg salt slag per ton of Al and 10-35 kg filter dust/t Al. Dross generated at ca. 25 kg/t Al can be reused in rotary drum furnaces (UBAVIE 2000).

Concentrations of PCDD/PCDF in filter dusts have been recorded from 3 to 18,000 ng TEQ/kg (SCEP 1994, Bremmer *et al.* 1994). Filter dusts are produced at a rate of approximately 8% of the metal production (Dyke *et al.* 1997). Combined with an average concentration of 5,000 ng TEQ/kg, this gives an emission factor of 400 µg TEQ/t of product for class 2 (fine particulates). Measurement data obtained both in the European Union (BREF 2009) and in China (Ba *et al.* 2009) from plants assigned to class 3 show concentrations of 4-5 ng TEQ/g of waste. Assuming the abovementioned 8% ratio, such concentrations correspond to an emission factor of 350-400 µg TEQ/t. Therefore, an emission factor of 400 µg TEQ/t is proposed for class 2.

The Italian study gave 183 µg TEQ/t and thus, the emission factor of class 1 has been changed to 200 µg TEQ/t of Al (ENEA 2003). Class 1 emission factor was confirmed. For class 3, optimized PCDD/PCDF control is implemented (including clean scrap), the lower factor of 100 µg TEQ/t should be applied to make initial estimates.

PCB concentrations measured at a Chinese plant related to class 2 were 0.4 ng TEQ/g of dust on average (Ba *et al.* 2009), which would correspond to an emission factor of 20 µg TEQ/t.

## Annex 21 Complementary information to source category 2f Lead Production

### Overview of recent revisions

The majority of PCDD/PCDF emission factors are confirmed for this source category except for class 3. A new emission factor has been assessed regarding class 4. Some new PCB and HCB emission factors are also proposed.

**Table III.21.1 PCB emission factors for source category 2f Lead Production**

2f Lead Production		Emission Factors ( $\mu\text{g TEQ/t lead}$ )				
Classification		Air	Water	Land	Product	Residue
1	Lead production from scrap containing PVC	2				
2	Lead production from PVC/Cl <sub>2</sub> free scrap, some APCS	0.2				0.1
3	Lead production from PVC/Cl <sub>2</sub> free scrap in highly efficient furnaces, with APC including scrubbers	0.002				
4	Pure primary lead production					

**Table III.21.2 HCB emission factors for source category 2f Lead Production**

2f Lead Production		Emission Factors ( $\mu\text{g/t lead}$ )				
Classification		Air	Water	Land	Product	Residue
1	Lead production from scrap containing PVC	1,000				
2	Lead production from PVC/Cl <sub>2</sub> free scrap, some APCS	1,000				
3	Lead production from PVC/Cl <sub>2</sub> free scrap in highly efficient furnaces, with APC including scrubbers	1,000				
4	Pure primary lead production	350				

Emission factors for PCB/HCB are provided with:

- A medium level of confidence for class 2 (PCB) and classes 3 and 4 (HCB), as emission factors are not based on expert judgment but are not derived from a broad geographical coverage;
- A low level of confidence for classes 1 and 3 (PCB) and classes 1 and 2 (HCB), as emission factors are based on extrapolations and expert judgment.

### Derivation of emission factors

#### Release to Air

Test data for production of lead from scrap materials are available from Germany (SCEP 1994, LUA 1997), Sweden, Belgium, the Netherlands (LUA 1997), and the USA (USEPA 2000b). In these countries, typically PVC is separated from batteries and facilities tested had dust abatement by fabric filters and some also had scrubbers. In US tests the addition of a scrubber reduced air emissions by approximately 90% (USEPA 2000b).

In the USA, the following emission factors were determined for the various types of secondary lead smelters (USEPA 2000b): Blast furnaces = 0.63-8.81  $\mu\text{g TEQ/t lead}$ , reverberatory/co-located furnace = 0.05-0.41  $\mu\text{g TEQ/t lead}$ , and rotary furnace = 0.24-0.66  $\mu\text{g TEQ/t lead}$ . Emissions to air were about 10-times higher before any scrubber/APCS than in the purified air. The average emissions were 8.31 and 0.63  $\text{ng TEQ/m}^3$  for blast furnaces before and after the scrubber, respectively; 0.41 and 0.05  $\text{ng TEQ/m}^3$  for reverberatories/collocated furnaces before and after the scrubbers, respectively; and 0.24 and 0.66  $\text{ng TEQ/m}^3$  for rotary kilns before and after the scrubbers, respectively.

European measurements gave 5  $\mu\text{g TEQ/t}$  of lead in Belgian blast furnaces and in the Netherlands for a lead smelter, which processed contaminated scrap but was equipped with lime injection and fabric filter (1.3  $\text{ng TEQ/m}^3$  were measured). German measurements were 0.14-0.27  $\text{ng TEQ/Nm}^3$  at rotary kilns; 0.59  $\text{ng TEQ/Nm}^3$  at a shaft furnace, 0.09-0.18  $\text{ng TEQ/Nm}^3$  at short rotary kilns and 0.14-0.27  $\text{ng TEQ/Nm}^3$  at rotary kilns. A recycling lead smelter for used car batteries had emissions between 0.2 and 0.3  $\text{ng TEQ/Nm}^3$ . The report, does not give average emission factors for the German secondary lead industry (LUA 1997). The Italian study reported an emission factor of 5.0  $\mu\text{g TEQ/t}$  of Pb for the production of secondary lead from pretreated vehicle batteries in rotary furnaces equipped with wet scrubbers.

The concentrations measured at the Thai secondary lead smelter (rotary kilns with afterburners, cyclone and bagfilter) ranged from 0.021 to 0.032  $\text{ng I-TEQ/m}^3$  with a mean of 0.027  $\text{ng I-TEQ/m}^3$  for the line with the combined flue gas streams and from 0.06 to 0.11  $\text{ng I-TEQ/m}^3$  with a mean of 0.089  $\text{ng I-TEQ/m}^3$  for line, which only operated the rotary kiln at the operational  $\text{O}_2$  content of about 19%. The latter concentration corresponds to an emission factor of 10  $\mu\text{g TEQ/t}$  of lead and therefore very well fits into class 2 (EF = 8  $\mu\text{g TEQ/t}$  of lead). Concentrations measured in China (Ba *et al.* 2009) led to an emission factor estimate of 0.64  $\mu\text{g TEQ/t}$ . The one calculated from measurements carried out in South Korea reaches 3.14  $\mu\text{g TEQ/t}$  (Yu *et al.* 2006). The CORINAIR database provides a higher emission factor of 20  $\mu\text{g TEQ/t}$  for secondary lead production sites where the efficiency of APC devices is low. Finally, data collected on three Japanese plants corresponding to class 3 were used to assess an emission factor of 0.06  $\mu\text{g TEQ/t}$  (Iwata *et al.* 2008).

An emission factor of 8  $\mu\text{g TEQ/t}$  of lead produced is to be used for furnaces fitted with fabric filters where PVC is excluded from battery separators (class 2). An estimated factor of 80  $\mu\text{g TEQ/t}$  is used where PVC may be present (class 1), this assessment being highly uncertain as no references are supporting it. For class 3, it is proposed to use an emission factor of 0.05  $\mu\text{g TEQ/t}$  for high technology furnaces and sophisticated flue gas cleaning equipment including scrubbers (concentrations well below 0.1  $\text{ng TEQ/m}^3$ ).

For primary lead production (class 4), an emission factor is proposed, based on measurement results from two plants in Japan (Iwata *et al.* 2008).

PCB air emissions from secondary lead production have been studied in China (Ba *et al.* 2009) and in South Korea (Yu *et al.* 2006). The former study derived an emission factor of 0.0037 µg TEQ/t, whereas the latter derived an emission factor of 0.31 µg TEQ/t. A mean value of 0.2 µg TEQ/t is thus proposed for class 2. Assuming that PCB emissions are lower than 10% of PCDD/PCDF emissions (expressed as TEQ), emission factors are proposed for class 1 (2 µg TEQ/t) and for class 3 (0.002 µg TEQ/t).

Regarding HCB air emissions, a Japanese reference gives emission factors of 990 µg/t for a lead recovery plant and of 340 µg/t for a lead primary melting plant (Iwata *et al.* 2008). Therefore a common emission factor of 1,000 µg/t is proposed for classes 1 to 3 and an emission factor of 350 µg/t for class 4.

### **Release to Water**

A release to water may result where effluents are discharged. There is not enough data to estimate an emissions factor. The presence of any liquid discharge should be noted and its source within the process recorded.

### **Release to Land**

No release to land is expected.

### **Release in Products**

No PCDD/PCDF is expected in the refined lead.

### **Release in Residues**

PCDD/PCDF will be present in flue gas treatment residues. Tests in Germany (SCEP 1994) reported concentrations between 2,600 and 3,100 ng TEQ/kg in dusts from a shaft furnace. Any use of residues as raw materials in other processes may result in transfer of PCDD/PCDF. An emission factor of 50 µg TEQ/t of Pb has been derived from the ENEA study (ENEA 2003). This emission factor has been confirmed by subsequent references from China (Ba *et al.* 2009) and South Korea (Jin *et al.* 2009).

PCB releases through residues have also been studied in China (Ba *et al.* 2009). Based on the emission factor reported in China, an emission factor of 0.1 µg TEQ/t is proposed for class 2.

## Annex 22 Complementary information to source category 2g Zinc Production

### Overview of recent revisions

For this source category, class 4 and 5 were merged together to include information on both zinc melting and primary zinc production. New PCDD/PCDF emission factors for residues were identified.

Emission factors for other unintentional POPs than PCDD/PCDF are presented below:

**Table III.22.1 PCB emission factors for source category 2g Zinc Production**

2g Zinc Production		Emission Factors (µg TEQ/t zinc)				
Classification		Air	Water	Land	Product	Residue
1	Kiln with no APCS	<b>100</b>				
2	Hot briquetting/rotary furnaces, basic dust control; <i>e.g.</i> , fabric filters/ESP	<b>2</b>				<b>3</b>
3	Comprehensive pollution controls, <i>e.g.</i> , fabric filters with active carbon/DeDiox technology	<b>0.1</b>				
4	Zinc melting and primary zinc production	<b>0.001</b>				

**Table III.22.2 HCB emission factors for source category 2g Zinc Production**

2g Zinc Production		Emission Factors (µg/t zinc)				
Classification		Air	Water	Land	Product	Residue
1	Kiln with no APCS	<b>50,000</b>				
2	Hot briquetting/rotary furnaces, basic dust control; <i>e.g.</i> , fabric filters/ESP	<b>50,000</b>				
3	Comprehensive pollution controls, <i>e.g.</i> , fabric filters with active carbon/DeDiox technology	<b>50,000</b>				
4	Zinc melting and primary zinc production	<b>1,000</b>				

Emission factors for PCB/HCB are provided with:

- A medium level of confidence for classes 1, 2 and 3 (PCB) and classes 3 and 4 (HCB), as emission factors are not based on expert judgment but are not derived from a broad geographical coverage;
- A low level of confidence for class 4 (PCB) and classes 1 and 2 (HCB), as emission factors are based on extrapolations and expert judgment.

### Derivation of emission factors

#### Release to Air



Emissions to air may arise from smelting processes and melting of mixed scrap. European plants would be fitted with fabric filter systems to control particulate emissions (HMIP 1994, LUA 1997).

In Germany, emission factors were provided for hot briquetting (63-379  $\mu\text{g TEQ/t}$  zinc with emissions between 89 and 953  $\text{ng TEQ/m}^3$ , mean = 521  $\text{ng TEQ/m}^3$ ), a rotating cylinder furnace (62.3  $\mu\text{g TEQ/t}$  with emissions between 10 and 335  $\text{ng TEQ/m}^3$ ; mean = 175  $\text{ng TEQ/m}^3$ ) and for zinc melting (typically under 0.1  $\text{ng TEQ/m}^3$  (LUA 1997).

Although this data set is very limited initial estimations of releases may be obtained by applying the emission factor of 100  $\mu\text{g TEQ/t}$  of zinc produced where hot briquetting or rotary furnaces are used (class 2). Where furnaces are used feeding scrap materials or filter ashes from the steel industry to recover zinc (Japanese data) and with no dust removal an estimated factor of 1,000  $\mu\text{g TEQ/t}$  can be used (class 1). For high technology facilities using comprehensive pollution controls such as fabric filters with lime and active carbon injection an estimated factor of 5  $\mu\text{g TEQ/t}$  can be used (class 3).

Class 1 emission factor has been confirmed by recent data obtained from a Waelz kiln in Taiwan which was not equipped with any APC (3,000  $\mu\text{g TEQ/t}$ , Chi 2009). In addition, the same paper confirmed class 2 emission factor from measurements on a Waelz kiln equipped with a scrubber, a cyclone and a bag filter (101  $\mu\text{g TEQ/t}$ ). It also measured an emission factor of 5  $\mu\text{g TEQ/t}$  on a plant equipped with a comprehensive APC (scrubber, cyclone, bag filter and activated carbon injection), confirming class 3 emission factor. Class 3 emission factor was also confirmed by Japanese data (7.1  $\mu\text{g TEQ/t}$ , Iwata *et al.* 2008).

In Japan, 10 measurements were achieved on different Zn primary melting plants (Iwata *et al.* 2008). The mean value was 0.11  $\mu\text{g TEQ/t}$ . Former classes 4 and 5 are merged into a new class 4 dedicated to zinc melting and primary zinc production.

The publication from Taiwan mentioned above (Chi *et al.* 2008) also allows for new PCB emission factors for classes 1 to 3. Class 4 PCB emission factor is derived from Polish data (Grochowalski *et al.* 2007).

Several Japanese publications (Iwata *et al.* 2008, Ota *et al.* 2005, Sakai *et al.* 2009) provided HCB emission factors for secondary zinc production (classes 1 to 3). Those ranged between 42,000 and 85,000  $\mu\text{g/t}$ . Therefore, an emission factor of 50,000 is proposed for these classes. The same publications also provided emission factors for primary zinc production (1,000  $\mu\text{g/t}$ ).

### **Release to Water**

A release may occur if effluents are discharged. The source of any effluent from the process should be noted.

### **Release to Land**

No release to land is expected.

### **Release in Products**

Levels of PCDD/PCDF in refined zinc are not relevant.

### **Release in Residues**

Residues from gas cleaning are expected to contain PCDD/PCDF. Three publications issued in 2009 gave first results focused on PCDD/PCDF levels in residues from secondary zinc production. In China, an emission factor of 0.246 µg TEQ/t zinc was derived (Ba *et al.* 2009). In South Korea, several plants were investigated without any process and APC description being given and an emission range of 0.02-13 µg TEQ/t zinc was provided. The third one was from a team from Taiwan which measured levels from residues produced by two Waelz kilns (260-1,900 µg TEQ/t EAF dust). Assuming 2 t EAF dust by ton of produced zinc, this range would correspond to emission factors of 520-3,200 µg TEQ/t zinc.

Therefore an emission factor of 0.02 µg TEQ/t zinc (lower end of Jin *et al.* 2007 range) is proposed for class 1. For classes 2 and 3, an emission factor of 1 µg TEQ/t zinc is proposed. However, in the specific case of Waelz kilns, emission factors can reach 2,000 µg TEQ/t zinc. The kind of process should therefore be cautiously recorded.

## Annex 23 Complementary information to source category 2h Brass and Bronze Production

### Overview of recent revisions

All PCDD/PCDF emission factors are confirmed for this source category. A new HCB emission factor is proposed with a medium level of confidence:

**Table III.23.1 HCB emission factors for source category 2h Brass and Bronze Production**

2h Brass and Bronze Production		Emission Factors ( $\mu\text{g}/\text{t}$ brass/bronze)				
Classification		Air	Water	Land	Product	Residue
1	Thermal de-oiling of turnings, afterburner, wet scrubber	9,400				
2	Simple melting furnaces					
3	Mixed scrap, induction furnaces, fabric filters	9,400				
4	Sophisticated equipment, <i>e.g.</i> induction ovens with APCS					

### Derivation of emission factors

#### Release to Air

Measured PCDD/PCDF data from brass production are available from the Thailand sampling program (UNEP 2001, Fiedler *et al.* 2002). The plant consisted of a small, batch-type smelter for primary and secondary brass production. The brass from the smelter was cast manually into bars, which were then rolled into coils for different products. The furnace was heated with about 30 L/h low sulfur, heavy fuel oil. The furnace was operated on a 250 kg/batch discontinuous mode during one day shift. The flue gases from the furnace and several surrounding areas pass a wet scrubber and are then discharged through the roof via a steel stack. Emissions to air may arise from smelting processes and melting of mixed scrap. The stack concentrations from the secondary brass smelter in Thailand ranged between 0.13 and 0.21 ng I-TEQ/Nm<sup>3</sup> with an average of 0.15 ng I-TEQ/Nm<sup>3</sup> at the actual operating O<sub>2</sub> concentration of 19%. This concentration corresponds to an emission factor of 11  $\mu\text{g}$  I-TEQ/t of brass (11  $\mu\text{g}$  WHO-TEQ/t). Hence, an emission factor of 10  $\mu\text{g}$  TEQ/t is assigned to class 2.

Emission factors developed for classes 1 and 3 in the 2005 version of the Toolkit have been confirmed by a Japanese study which derived an emission factor of 1.7  $\mu\text{g}$  TEQ/t from 16 measurements (Iwata *et al.* 2008). In addition, the emission factor developed for class 4 in the 2005 version of the Toolkit has been confirmed by data from New Zealand. Measurements carried out on an induction furnace equipped with a bag filter showed concentrations ranging from 0.0053 to 0.017 ng TEQ/Nm<sup>3</sup>, corresponding to an emission factor range of 0.03 to 0.14  $\mu\text{g}$  TEQ/t (Merz 2004).

As far as HCB is concerned, the Japanese study provides an emission factor value of 9,400  $\mu\text{g}/\text{t}$ , based on the same 16 measurements. This value is proposed as a Toolkit emission factor for classes 1 and 3.

### **Release to Water**

A release may occur if effluents are discharged. The source of any effluent from the process should be noted.

### **Release to Land**

No release to land is expected.

### **Release in Products**

Levels of PCDD/PCDF in refined brass are not relevant.

### **Release in Residues**

Residues from gas cleaning as well as in sludge from wet scrubbers, if present, are expected to contain PCDD/PCDF. The PCDD/PCDF concentrations in the sludge samples taken from the clarifier of the water treatment system of the wet scrubbers were rather high with 8,683 and 8,567 ng I-TEQ/kg d.m., respectively. In most countries, residues from such processes or with such concentrations would be classified as hazardous waste. The amount of sludge generated was low but could not be quantified. As expected, the slag sample from the furnace exhibited a low concentration of 13.6 ng I-TEQ/kg (UNEP 2001, Fiedler et al. 2002). There is still insufficient information to provide emission factors for solid residues.

## Annex 24 Complementary information to source category 2i Magnesium Production

### Overview of recent revisions

All PCDD/PCDF emission factors are confirmed for this source category. Some new emission factors are proposed for PCBs and HCB with a medium level of confidence.

**Table III.24.1 PCB emission factors for source category 2i Magnesium Production**

2i Magnesium Production		Emission Factors (µg TEQ/t magnesium)				
Classification		Air	Water	Land	Product	Residue
1	Production using MgO/C thermal treatment in Cl <sub>2</sub> – no treatment on effluent, limited gas treatment					
2	Production using MgO/C thermal treatment in Cl <sub>2</sub> – comprehensive pollution control	0.7				
3	Thermal reduction process	0.02				

**Table III.24.2 HCB emission factors for source category 2i Magnesium Production**

2i Magnesium Production		Emission Factors (µg/t of magnesium)				
Classification		Air	Water	Land	Product	Residue
1	Production using MgO/C thermal treatment in Cl <sub>2</sub> – no treatment on effluent, limited gas treatment					
2	Production using MgO/C thermal treatment in Cl <sub>2</sub> – comprehensive pollution control					
3	Thermal reduction process	800				

### Derivation of emission factors

#### Release to Air

Emission factors to air from the production of magnesium by using the chlorination electrolytic process are quite uncertain. PCDD/PCDF are formed and released from the chlorination furnace where magnesium oxide is converted into magnesium chloride. The following data are reported in the EU BREF document: 0.8 ng TEQ/Nm<sup>3</sup> were found from chlorination off-gas treatment (EF = 12 µg TEQ/t); for the vent gases from chlorination, an emission factor of 28 µg TEQ/t was determined and concentrations in the hall from electrolysis and chlorination gave an emission factor of 13 µg TEQ/t (BREF 2009).

An emission factor of 250 µg TEQ/t of production is estimated for electrolytic processes, which do not have afterburners but use wet scrubbers (class 1). For processes with multi-stage wet scrubbers and afterburners an emission factor of 50 µg TEQ/t of production (class 2). This emission factor is confirmed by data from China where PCDD/PCDF concentrations ranging from 6.5 to 13.2 pg TEQ/Nm<sup>3</sup> were measured on two plants. Using production data and gas flows reported in the paper, emission factors

can be derived (6 and 23 µg TEQ/t). In 2010, an emission factor of 0.41 µg TEQ/t was reported by the same team (Nie *et al.* 2010).

For plants applying the thermal reduction process (class 3), an emission factor of 3 µg TEQ/t will be used (BREF 2009).

Emissions could be much higher if the gas treatment is limited or where a high PCDD/PCDF producing carbon source is used. Indeed, one of the Chinese sources mentioned above reported concentrations of 10.1 pg TEQ/Nm<sup>3</sup> which, combined with an uncommon low production flow (1 kg/h), corresponds to a high emission factor (assumed to be higher than 500 µg TEQ/t).

Regarding air emissions of PCBs and HCB, emission factors were assessed in China and are available for installations falling under both classes 2 and 3 (Nie *et al.* 2010).

### **Release to Water**

Releases to water will depend on the amount of PCDD/PCDF formed in the process, the efficiency of the scrubbing systems to remove PCDD/PCDF in gas streams and crucially on the treatment applied to the effluents.

There is insufficient information to estimate releases from processes other than those including a thermal treatment of MgO/coke in Cl<sub>2</sub>.

For processes fitted with comprehensive water treatment (including high efficiency solids removal), an emission factor is estimated based on releases reported from the Norwegian plant in the late 1990s or under 1 g TEQ per year. Prior to the installation of the water treatment system releases to water were estimated at 500 g TEQ per year and this is used to estimate an emission factor to be used where no treatment occurs.

An emission factor of 9,000 µg TEQ/t of Mg is used where direct discharge of the untreated effluent occurs. From European plants, an emission factor of 33 µg TEQ/t of Mg metal was reported (BREF 2009).

### **Release to Land**

A release to land may occur where part of the water treatment involves release to a lagoon. Quantities are estimated in the residue section.

### **Release in Products**

PCDD/PCDF levels in magnesium produced are expected to be negligible.

### **Release in Residues**

Residues from scrubbing processes may be expected to contain PCDD/PCDF. A stage in the water treatment may include settling in a lagoon, which would constitute a release of the residue to land. To estimate the release from the electrolytic process, it can be assumed that 0.01 ton of PCDD/PCDF-containing sludge is generated in the water treatment plant (BREF 2009).

Very little information is available on the concentrations of PCDD/PCDF in residues from this process or the amounts of residue produced. Initial estimates only may be made.

It is assumed that where no water treatment is used, no PCDD/PCDF is found in residues (although some may arise from other parts of the process). So the emission factor is zero. Where comprehensive water treatment is applied it is assumed that the difference in the release to water will approximately equal the PCDD/PCDF captured and therefore be present in the residues. An emission factor of about 9,000 µg TEQ/t of production is given to make an initial estimate.

## **Annex 25 Complementary information to source category 2j Other Non-ferrous Metal Production**

### **Overview of recent revisions**

No revisions of emission factors have been made. Additional guidance has been introduced on classifying sources within this category, estimating activity rates, and on data quality aspects.

### **Derivation of emission factors**

#### **Release to Air**

Work in Norway showed that a process carried out to refine primary nickel, which used a fluidized bed reactor at 800°C to convert NiCl<sub>2</sub> to NiO, had polluted the environment heavily with PCDD/PCDF but no emission factors were given (Oehme *et al.* 1989).

Tests in Germany have identified high emissions from tin smelting (up to 113 µg TEQ/t) but insufficient information is provided to be able to apply this emission factor to tin production processes in general (Bröker *et al.* 1999).

Other thermal metal processes can release PCDD/PCDF and emissions will be influenced by the degree of contamination on the scrap materials and the capture and treatment of the flue gases. Lowest emissions can be expected where the raw materials are clean and gas treatment comprehensive – including dust control by fabric filters, lime injection and possibly activated carbon addition and in some cases an afterburner.

Emissions will be high for installations with poor controls on input materials leading to high concentrations. Even if mass flow is small, local contamination may result. The emission factors are estimated based on patchy data on thermal non-ferrous metal recovery, concentrations would vary widely from well under 1 ng/m<sup>3</sup> (class 2) to tens of ng/m<sup>3</sup> (class 1).

#### **Release to Water**

Releases to water may occur where effluents are discharged. The presence and source of effluents should be noted.

#### **Release to Land**

No release is expected except where residues are dumped on land.

#### **Release in Products**

No PCDD/PCDF is expected in refined metal products.

#### **Release in Residues**

Residues may contain PCDD/PCDF. Insufficient data were available to estimate emissions factors. The use of a residue as a raw material could lead to contamination of the subsequent process.



## Annex 26 Complementary information to source category 2k Shredders

### Overview of recent revisions

For this source category, PCDD/PCDF emission factors for air were confirmed, while a new emission factor was proposed for residues. New emission factors are also proposed for PCBs.

**Table III.26.1 PCB emission factors for source category 2k Shredders**

2k Shredders		Emission Factors ( $\mu\text{g TEQ/t}$ recovered steel)				
Classification		Air	Water	Land	Product	Residue
1	Metal shredding plants	0.4				15

Emission factors for air emissions are provided with a high level of confidence, as these are derived from a broad geographical coverage and are based on a low data range and not on expert judgment. Emission factors for residues releases are provided with a low level of confidence, as these are based on extrapolations and expert judgment.

### Derivation of emission factors

#### Release to Air

Emissions arise due to the presence of PCB and PCDD/PCDF contained in the feed to the shredder plants such as motor vehicles, household electrical equipment, or other electrical appliances, and are released to the air by the mechanical destruction. An emission factor of  $0.2 \mu\text{g TEQ/t}$  (concentration of  $0.04\text{-}0.4 \text{ ng TEQ/m}^3$ ) is developed based on data provided by SCEP (1994). This emission factor is confirmed by two other European publications (Schleicher *et al.* 2009, François *et al.* 2005). Mean concentrations of  $0.14 \text{ ng TEQ/Nm}^3$  and  $0.023 \text{ ng TEQ/Nm}^3$  (10 samples) were measured respectively. Assuming a production of  $80 \text{ t/h}$  and a gas flow of  $65,000 \text{ Nm}^3/\text{h}$ , such concentrations would correspond to emission factors ranging from  $0.019$  to  $0.30 \mu\text{g TEQ/t}$  of recovered steel.

These two publications also give PCB measurement data. The Belgian one (10 samples from 3 plants) shows concentrations from  $0.025$  to  $0.74 \text{ ng TEQ/Nm}^3$  which would correspond to a mean emission factor of  $0.32 \mu\text{g TEQ/t}$ . The Swedish one (10 samples) show concentrations ranging from  $0.29$  to  $0.94 \text{ ng TEQ/Nm}^3$ , corresponding to a mean emission factor of  $0.45 \mu\text{g TEQ/t}$  of recovered steel. Therefore, a PCB emission factor of  $0.4 \mu\text{g TEQ/t}$  is proposed for the purpose of the Toolkit.

The fact that PCB emission factors are higher than PCDD/PCDF emission factors should be highlighted.

#### Release to Water

A release to water could occur where effluents are discharged. No data were available to estimate emission factors. Any liquid discharge should be reported and any treatment applied.

#### Release to Land

No release to land is expected.

### **Release in Products**

It is likely that the products will have some level of contamination on them although it is not possible to estimate this.

### **Release in Residues**

Residues may be materials from dust removal devices or unsellable products from the shredding operation (non-metallic materials). The Belgian study mentioned above also reported data on PCDD/PCDF releases through residues. A value of 0.023 ng TEQ/g of residue is reported. Assuming a release of 200 kg of residues/t of product, such a concentration would correspond to a PCDD/PCDF emission factor of 5 µg TEQ/t of recovered steel. A new emission factor is suggested for PCB from Danish data (Schleicher *et al.* 2009).

## Annex 27 Complementary information to source category 2I Thermal Wire Reclamation and E-waste Recycling

### Overview of recent revisions

Category 2I was revised to specifically include e-waste recycling. A new class was added to cover open burning of circuit boards (new class 2). Some new emission factors for PCBs are also proposed with a medium level of confidence.

**Table III.27.1 PCB emission factors for source category 2I Thermal Wire Reclamation and E-waste Recycling**

2I Thermal Wire Reclamation and E-waste Recycling		Emission Factors ( $\mu\text{g TEQ/t material}$ )				
		Air	Water	Land	Product	Residue
1	Open burning of cable	400				
2	Open burning of circuit boards	3				
3	Basic furnace with afterburner and wet scrubber					
4	Burning electric motors and brake shoes, etc. – afterburner fitted					

### Derivation of emission factors

#### Release to Air

To our knowledge, there are no measured data for emissions from open cable burning and only very few from legal cable burners. Highest concentrations reported for thermal wire reclamation were 254 ng TEQ/m<sup>3</sup> (Dutch data) and emission factors up to 500  $\mu\text{g TEQ/t}$  were used in the Dutch and Austrian inventories (LUA 2000); lowest were 3.3  $\mu\text{g TEQ/t}$ . The Swiss inventory applied an emission factor of 2,340  $\mu\text{g TEQ/t}$  (LUA 2000). A literature review and additional experiments carried out in the USA gave very different emission factors for cables on the one hand and circuit boards on the other hand: 28-155  $\mu\text{g TEQ/t}$  for the former and 5,400-18,100 for the latter (Gullett *et al.* 2007). Experiments achieved in Japan on cable burning showed similar emission factors (Shibata *et al.* 2003). Therefore, a new class 2 assigned to open burning of circuit boards is proposed. New emission factors for class 1 (open burning of cables) and class 2 (open burning of circuit boards) are proposed to be 12,000  $\mu\text{g TEQ/t}$  and 100  $\mu\text{g TEQ/t}$  respectively.

Class 2 emission factors should be used for cable burning in furnaces fitted with afterburners and wet scrubbers. The concentration of 40  $\mu\text{g TEQ/t}$  for emissions to air was given by Bremmer *et al.* (1994).

For furnaces burning electric motors, brake shoes and the like and fitted with an afterburner an emission factor of 3.3  $\mu\text{g TEQ/t}$  is used (Bremmer *et al.* 1994). Any similar recovery operations should be looked at and a note made of the controls applied and any gas cleaning in use.

Dioxin-related compounds in house dust from Vietnamese e-waste recycling sites were characterized and it was shown that PCBs accounted for 3% of the PCDD/PCDF TEQ (Tue *et al.* 2010). Based on that

results and on the proposed emission factors for PCDD/PCDF, the following emission factors for PCBs are proposed for classes 1 and 2: 400 and 3 µg TEQ/t respectively.

### **Release to Water**

Where a furnace is used and a wet scrubber is present a release to water is expected. The presence of wet scrubber systems at such plants should be noted, the fate of effluent and any treatment applied to the effluent noted. No data has been found to derive emission factors.

### **Release to Land**

Releases to land are expected to occur where open processing takes place, the residues in this case will be on the ground. At illegal burning sites, soil concentrations up to 98,000 ng TEQ/kg have been measured. In other cases where residues are removed these will be considered in the Section on residues. In the case of open cable burning contamination of the land can be significant and sites should be identified as potential hotspots.

### **Release in Products**

No release into the copper product is expected.

### **Release in Residues**

Residues from the process are expected to contain PCDD/PCDF and levels may be high. No data were available to estimate releases.

## Annex 28 Heating Values and Biomass Ash Contents

The basis for reporting default Toolkit emission factors is the energetic output. For this, the Toolkit refers to TJ (Terajoules) and not to the mass in tons of feed material. In cases where mass consumption data are available, the following tables provide indicative relation of masses (in kg) to heat outputs (in MJ).

**Table III.28.1 Heating values for coal**

Type of Coal	Heating Value
Anthracite, Germany	27–35 MJ/kg depending on the mine
Bituminous coal, France	32–34 MJ/kg
Bituminous coal, USA	31–32 MJ/kg
Anthracite, Russia	30 MJ/kg (Donez Bay)
Bituminous coal, Germany	29–32 MJ/kg
Bituminous coal, China	25–27 MJ/kg
Bituminous coal, Poland	20.5-30.5 MJ/kg
Sub-bituminous coal, Spain	16–17 MJ/kg
Sub-bituminous coal, Croatia	13–15 MJ/kg
Sub-bituminous coal, Turkey	12–14 MJ/kg
Lignite/brown coal, Germany (Central)	10–12 MJ/kg
Lignite/brown coal, Czech Republic	9–11 MJ/kg
Lignite/brown coal, Germany (West)	8–10 MJ/kg
Lignite/brown coal, Australia	8–9 MJ/kg
Lignite/brown coal, Germany (East)	7–9 MJ/kg
Lignite/brown coal, Greece	4–6 MJ/kg

**Table III.28.2 Heating values for coke**

Type of Coke	Heating Value
Swell coke, Czech Republic	31–32 MJ/kg
Anthracite coke, Germany	28–30 MJ/kg
Lignite coke, Germany	27–28 MJ/kg
Swell coke, Germany	23–25 MJ/kg

**Table III.28.3 Heating values for oil**

Type of Oil	Heating Value
Gasoline	44–47 MJ/kg
Light fuel oil/Diesel fuel	43–46 MJ/kg
Heavy fuel oil	40–43 MJ/kg
Lignite tar oil	38–40 MJ/kg

Anthracite tar oil	37–39 MJ/kg
Ethanol	29 MJ/kg
Oil shale (from Estonia)	8-10 MJ/kg

**Table III.28.4 Heating values for gas**

Type of Gas	Heating Value
Methane	50 MJ/kg
Ethane	47 MJ/kg
Propane	46 MJ/kg
Butane	46 MJ/kg
Natural gas, North Sea – Great Britain	48–53 MJ/kg
Natural gas, North Sea-Germany	47–52 MJ/kg
Natural gas class H	46–50 MJ/kg
Natural gas class L	44–49 MJ/kg
Natural gas, The Netherlands	40–45 MJ/kg
Methanol	38–44 MJ/kg
Carbon monoxide	20 MJ/kg
For a first estimate, mean values should be applied as follows	10MJ/kg
Natural gas	48 MJ/kg
LPG (mean heating value)	46 MJ/kg

**Table III.28.5 Heating values for wood**

Type of Wood	Heating Value
Spruce, air dry	14–17 MJ/kg
Poplar, air dry	15–16 MJ/kg
Beech, air dry	13–15 MJ/kg
Beech, green	12–13 MJ/kg
Beech bark	11–13 MJ/kg
Spruce bark	10–12 MJ/kg

**Table III.28.6 Heating values for biomass**

Type of Biomass	Heating Value
Coconut shells	17–19 MJ/kg
Almond shells	17–19 MJ/kg
Peat Pellets	15–18 MJ/kg
Peat, Germany	15–17 MJ/kg
Straw (wheat)	15–17 MJ/kg
Coconut fibers	14–16 MJ/kg

Rice husks	14–15 MJ/kg
Coffee roasting residue	9–11 MJ/kg
Peat, Finland	9–11 MJ/kg
Bagasse	8–10 MJ/kg
Peat, Spain	1–3 MJ/kg

The following correlations exist for converting energy and power units:

**Table III.28.7 Selected correlations for energy and power units**

<b>Energy</b>		<b>Corresponds to:</b>	
Watt hour (Wh)	1	3,600	Joule (J)
	1	3.6	Kilojoule (kJ)
	1	0.0036	Megajoule (MJ)
Kilowatt hour (kWh)	1	3,600,000	Joule (J)
	1	3,600	Kilojoule (kJ)
	1	3.6	Megajoule (MJ)
	1	$3.6 \times 10^{-6}$	Terajoule (TJ)
Gigawatt hour (GWh)	1	3.6	Terajoule (TJ)
Terajoule (TJ)	1	2,777,777,778	Kilowatt hour (kWh)
<b>Power</b>			
Watt (W)	1	1	Joule per second (J/s)
	1	60	Joule per minute (J/min)
	1	3,600	Joule per hour (J/h)
Megawatt (MW)	1	1,000,000	Joule per second (J/s)

**Table III.28.8 Selected conversion factors and energy equivalents for Group 3 Power Generation and Heating**

<b>WEC* Standard Energy Units</b>	<b>equals</b>	
1 tonne of oil equivalent (toe) **	42 000	MJ (net calorific value)
1 tonne of coal equivalent (tce)	29300	MJ (net calorific value)
<b>Representative Average Conversion Factors</b>		
1 ton of natural gas liquids	45000	MJ (net calorific value)
1,000 standard cubic meter of natural gas	36000	MJ (net calorific value)
1 ton of peat	0.2275	toe
1 ton of fuelwood	0.3215	toe
1 kWh (primary energy equivalent)	9.36	MJ
<b>Electricity</b>		
1 kWh of electricity output	3.6	MJ

\* World Energy Council

\*\* ton of oil equivalent currently employed by the International Energy Agency and the United Nations Statistics Division, defined as 107 kilocalories, net calorific value (equivalent to 41.868 GJ)

**Table III.28.9 Ash contents of various woods, dry basis (% mass)**

Type	Wood/other	Bark	Reference
Douglas fir	0.1-0.8	1.2-2.2	Beauchemin and Tempier (2008)
Western hemlock	0.2-2.1	1.7-3.7	Beauchemin and Tempier (2008)
Ponderosa pine	0.2	0.7	Beauchemin and Tempier (2008)
Lodgepole pine	2.5	2.0	Beauchemin and Tempier (2008)
Spruce	3.0	3.8	Beauchemin and Tempier (2008)
Redwood	0.2	0.4-0.8	Beauchemin and Tempier (2008)
Cedar	0.2	0.2	Beauchemin and Tempier (2008)
Coniferous wood	0.3	4.0	Obernberger (2006)
Deciduous wood	0.3	5.0	Obernberger (2006)
Straw from wheat, ray, barley, oilseed rape	5.0	-	Obernberger (2006)
Grains from wheat, rye, barley	5.0	-	Obernberger (2006)
Grains from rape	2.0	-	Obernberger (2006)
Grass, in general	7.0	-	Obernberger (2006)
Miscanthus (China reed)	4.0	-	Obernberger (2006)



## Annex 29 Conversion Factors for Liquid and Gaseous Fuels

Very often, consumption numbers for gasoline and Diesel in transportation or crude oil in the energy sector may be given in liters (L). Further, consumption numbers for gaseous fuels, such as natural gas, may be given in cubic meters (m<sup>3</sup>). For the Toolkit, these volumes have to be converted into tons or heating values. For the purpose of the Toolkit:

- 1 L of gasoline has a mass of about 0.74 kg; thus, a conversion factor of 0.00074 must be used to convert liters of gasoline into tons;
- 1 L of (normal) Diesel fuel (for automobiles, trucks, etc.) and/or light fuel oil (including heating oil) has a mass of about 0.85 kg; thus, a conversion factor of 0.00085 must be used to convert liters of Diesel and/or light fuel oil into tons;
- 1 L of heavy duty fuel has a mass of about 0.970 kg; thus, a conversion factor of 0.00097 must be used to convert liters of heavy duty fuel into tons;
- 1 m<sup>3</sup> of natural gas has a mass between 0.77 and 0.85 kg; with a mean of 0.8 kg; thus, a conversion factor of 0.0008 must be used to convert m<sup>3</sup> of natural gas into tons; a conversion factor of 0.0000008 must be used to convert liters of natural gas into tons;
- 1 m<sup>3</sup> of LPG (mixture of propane and butane) has a mass of about 2 kg; thus, a conversion factor of 0.002 must be used to convert m<sup>3</sup> of LPG into tons and a conversion factor of 0.000002 must be applied to convert liters of LPG into tons.

### Specific flue gas volume (SFV)

The SFV represents the specific dry flue gas flow of the fuel at reference oxygen. Typical SFV values are:

Coal (O <sub>2</sub> ref = 6%)	SFV = 350 Nm <sup>3</sup> /GJ
Fuel oil (O <sub>2</sub> ref = 3%)	SFV = 280 Nm <sup>3</sup> /GJ
Natural gas (O <sub>2</sub> ref = 3%)	SFV = 270 Nm <sup>3</sup> /GJ

(N: Normal conditions: 0.1013 MPa, 273K)

These fuel dependent specific flue gas volumes shall be converted for different reference oxygen concentrations, for instance:

Stationary diesel engines with O <sub>2</sub> ref = 5%	SFV = 315 Nm <sup>3</sup> /GJ
Stationary gas turbines burning domestic oil with O <sub>2</sub> ref = 15%	SFV = 840 Nm <sup>3</sup> /GJ
Stationary gas turbines burning natural gas with O <sub>2</sub> ref = 15%	SFV = 810 Nm <sup>3</sup> /GJ

The SFV may also be calculated from the fuel analysis if available. However it should be noted that the SFV depends only slightly on the fuel when expressed in Nm<sup>3</sup>/GJ.

### Calculating emission factors from given concentrations (VGB/EURELECTRIC 2010):

$$EF = C \times SFV / 1,000$$

EF: Emission factor (g/GJ)

C: Concentration in the dry flue gas at reference oxygen content (mg/Nm<sup>3</sup>)

## Annex 30 Complementary information to source category 3a Fossil Fuel Power Plants

### Overview of recent revisions

Approximately ninety literature sources have been identified in a worldwide search for primary measurement data and emission factors for fossil fuel fired power plants. Investigations included air emissions and releases into residues. The revision of the information related to source group 3 focused on the following aspects:

- Review of existing emission factors
- Review of proposed source categories
- Further information to be included on non- conventional fuels
- Derivation of emission factors for „simple“ technologies

In source category 3a “Fossil fuel power plants”, a new class was introduced and a new dioxin emission factor was proposed to cover releases from peat fired power boilers. The proposed emission factor refers to peat combustion in boilers for heat and/or power production. Peat is used in countries where it is domestically available. As for class 2 covering coal fired power boilers, it should be noted that the use of high-chlorine coal induces higher releases to air, of up to 200 µg TEQ/TJ.

### Derivation of emission factors

#### Release to Air

Releases to air are the predominant vector for fossil fuel combustion. Typically, measured concentrations from large power plants are far below 0.1 ng TEQ/m<sup>3</sup>; mostly one to two orders of magnitude for solid and liquid fuels. Whereas Dutch data from large coal-fired power plants gave an emission factor of 0.35 µg TEQ/t, German data were between 0.004 and 0.2 µg TEQ/t (0.09 and 7.1 µg TEQ/TJ) and UK data had a median value of 0.14 µg TEQ/t (range: 0.06-0.32 µg TEQ/t). Swiss sources gave mean emission factors of 230 µg TEQ/TJ for coal-fired power plants. German data report between 0.02 and 0.03 µg TEQ/TJ for natural gas-fired boilers (LUA 1997).

The default emission factor for class 1 was derived from values reported between 0.4 and 118 µg TEQ/TJ. For the Toolkit, a median value of 35 µg TEQ/TJ was chosen. Class 2 emission factor was derived from average values reported between 230 (Swiss data from LUA 1997) and 7 µg TEQ/TJ. The reported values vary in a broad range from 3 -100 µg TEQ/TJ and depend highly on fuel quality and power plant technology. The lower end refers to measurements at a coal-fired power plant in Poland with circulating fluidized bed technology (Grochowalski and Konieczynski 2008).

Class 3 emission factor was derived based on McGettigan (2009). Class 4 was derived from average values reported between 1 and 4 µg TEQ/TJ. Class 5 is based from emission measurements taken at two power plants in Estonia firing shale oil, which gave emissions between 2.3 and 24 pg I-TEQ/Nm<sup>3</sup> (at 10% O<sub>2</sub>). The comparatively high concentration of 400 pg I-TEQ/Nm<sup>3</sup> (at 10% O<sub>2</sub>) has not been taken into account when determining the emission factor due to operational problems at the plant (Schleicher *et*

*al.* 2004a). Class 6 emission factor came from average values reported between 0.5 and 1.5 µg TEQ/TJ (LUA 1997, IFEU 1998, Environment Canada 1999).

### **Release to Water**

No release to water is expected. However, in cases where wet scrubbers are installed and effluents are generated, this release vector needs to be highlighted. Presently, no numeric value can be provided to estimate this release.

### **Release to Land**

No release to land is expected unless untreated residue is directly placed onto or mixed with soil.

### **Release in Products**

The process has no product; thus no release to product occurs.

### **Release in Residues**

There is a scarcity of measured data for PCDD/PCDF concentrations in fly ash and more data will be needed. It can be assumed that the content of PCDD/PCDF in the fly ash increases with the content of unburned carbon and the amount of waste co-fired.

Estonia, where power plants use shale oil as a fuel, PCDD/PCDF have been analyzed in fly ashes from power plants, which were equipped with electrostatic precipitators. The concentrations in these fly ashes ranged from non quantifiable concentrations to 1.66 ng I-TEQ/kg of dry ash (LOQ included for TEQ calculation) (Schleicher *et al.* 2004a, Roots 2001). The data do not enable determination of emission factor and thus, countries that wish to quantify the releases from the power plants fuelled with shale oil and are equipped with ESPs, may wish to multiply the mean of the above two measurements (= 1.2 g TEQ/t of ESP fly ash) with the mass of fly ash collected from these plants.

To make a preliminary estimate, UK data on PCDD/PCDF in residues from industrial coal combustion can be used (Dyke *et al.* 1997, EC 1999a). Concentrations in fly ash were 0.23-8.7 ng TEQ/kg ash and grate ash gave 0.02-13.5 ng TEQ/kg. The concentrations in soot were higher (up to 53 ng TEQ/kg). Taking an average ash production rate of 10% and average concentration of 4 ng TEQ/kg ash, an emission factor of 0.4 µg TEQ/t (coal input) (approx. 14 µg TEQ/TJ) was derived.

## Annex 31 Complementary information to source category 3b Biomass Power Plants

### Overview of recent revisions

Two new classes were added to category 3b Biomass power plants, *i.e.* straw fired boilers as class 3 and boilers fired with bagasse, rice husk, etc. as class 4. Straw-fired boilers need to be adapted to this fuel with regard to ash properties (slagging) and combustion conditions. Due to the chlorine content of straw, PCDD/PCDF emissions are expected to be higher than clean wood. As for boiler fired with various types of herbaceous biomass such as rice husk or bagasse, these are especially used in Asian countries, along with a wide range of agricultural residues. Nevertheless, information on PCDD/PCDF emissions from this source is still scarce.

### Derivation of emission factors

#### Release to Air

Releases to air are the predominant vector for biomass combustion. The default emission factor for class 1 was derived from average values for straw combustion reported for the UK ranging between 17 and 54 µg TEQ/t. Data reported from Austria ranges between 2–500 µg TEQ/TJ. Based on an average heating value of about 8–11 MJ/kg a default emission factor of 500 µg TEQ/TJ was chosen as a representative value even though values as high as 5,000 µg TEQ/TJ could be found. Class 2 was derived from mean values reported between 4.7 (Belgian study) and 5.4 (UK study) µg TEQ/t of wood burned. Based on an average heating value of 12–15 MJ/kg, a default emission factor of about 350 ng TEQ/GJ can be calculated. (LUA 1997, IFEU 1998, Environment Canada 1999). The factor of class 3 characterizing emissions into the air is based on Schleicher (2002). As no reference for emissions into the air is available for class 4, the factor derived for straw is proposed as a first expert estimate.

#### Release to Water

No release to water is expected. However, in cases where wet scrubbers are installed and effluents are generated, this release vector needs to be highlighted. Presently, no numeric value can be provided to estimate this release.

#### Release to Land

No release to land is expected unless untreated residue is directly placed onto or mixed with soil.

#### Release in Products

The process has no product; thus no release to product occurs.

#### Release in Residues

PCDD/PCDF in the ash residue can be assumed to be present. However, very limited detailed data regarding the amounts could be found. Based on a German study, typical concentrations range from 30–3,000 ng TEQ/kg for bottom ash and 30–23,300 ng TEQ/kg for fly ash. Due to the large overlap in values reported for bottom ash and fly ash, no further differentiation was deemed necessary. Thus, an average value of 3,000 ng TEQ/kg based on an ash content of 0.5% was chosen as a default emission factor. New

emission factors are proposed for residues in class 3 derived from Nielsen (2003). The class 4 emission factor for releases through residues is based on Choong Kwet Yive (2008).

## **Annex 32 Complementary information to source category 3c Landfill Biogas Combustion**

### **Overview of recent revisions**

No revisions of emission factors have been made for this source category. Additional guidance has been introduced on classifying sources within this category, estimating activity rates, and on data quality aspects.

### **Derivation of emission factors**

#### **Release to Air**

Releases to air are the only vector for landfill gas and biogas combustion. The default emission factor was derived from mean values reported between 7.6 and 8.4 µg TEQ/TJ of biogas burned as a mean value for the German and UK study, respectively (LUA 1997, IFEU 1998, Environment Canada 1999). Emissions in the German studies ranged from 0.001 to 0.28 ng I-TEQ/m<sup>3</sup>, Dutch measurements gave 0.07 ng I-TEQ/m<sup>3</sup> (LUA 1997). A recent study from Belgium reported PCDD/PCDF concentrations below 0.1 g I-TEQ/Nm<sup>3</sup> (at 5% O<sub>2</sub>) for measurements of flared biogas at five landfill sites (Idczak *et al.* 2004).

#### **Release to Water**

No release to water is expected.

#### **Release to Land**

No release to land is expected since landfill gas and biogas burn virtually residue-free.

#### **Release in Products**

The process has no product; thus no release to product occurs.

#### **Release in Residues**

No release to residue occurs since landfill gas and biogas burn virtually residue-free.

## Annex 33 Complementary information to source category 3d Household Heating and Cooking with Biomass

### Overview of recent revisions

In source category 3d “Household heating and cooking with biomass”, the information generated within the pilot project on simple stoves in Mexico is included; the experiment used an indoor high-volume sampler and one continuous sampler, as well as an outdoor sampler. The results of this pilot project, including measurements of PCDD/PCDF, PCB and HCB emissions from four simple stoves using wood as fuel, with limited combustion control and a duct for the evacuation of flue gases, were used to revise and amend emission factors to air and residues. Results obtained suggest daily fluctuations of PCDD/PCDF levels according to the cooking pattern.

Four new classes were added in this category, as follows:

- Straw fired stoves, including all types of residential combustion using herbaceous biomass as a fuel such as straw pellets.
- Charcoal fired stoves, including all types of residential combustion using charcoal as a fuel. Higher emissions may nevertheless occur from barbecuing.
- Open-fire (3-stone) stoves (virgin wood), including residential combustion of wood without control of combustion conditions and without ducts for the evacuation of flue gases. Traditional 3-stone stoves are a typical example.
- Simple stoves (virgin wood) used for cooking with limited combustion control and with a duct for the evacuation of flue gases.

Emission factors for dioxin like PCB,  $\Sigma$ 6PCB and HCB are proposed for two classes in this category, *i.e.* open-fire 3-stone stoves (virgin wood) and simple stoves (virgin wood), based on the results of the project in Mexico (Cardenas *et al.* 2011).

**Table II.33.1 Dioxin-like PCB in WHO 2005 TEQ emission factors for source category 3d Household Heating and Cooking with Biomass**

3d	Household Heating and Cooking with Biomass	Emission Factors ( $\mu\text{g TEQ/TJ}$ )				
		Air	Water	Land	Product	Residue ng/kg
5	Open-fire 3-stone stoves (virgin wood)					0.1
6	Simple stoves (virgin wood)	10	0		0	0.1

**Table II.33.2  $\Sigma$ 6PCB emission factors for source category 3d Household Heating and Cooking with Biomass**

3d	Household Heating and Cooking with Biomass	Emission Factors (mg/TJ)
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Classification		Air	Water	Land	Product	Residue ng/kg
5	Open-fire 3-stone stoves (virgin wood)					
6	Simple stoves (virgin wood)	100	0		0	ND

**Table II.33.3 HCB emission factors for source category 3d Household Heating and Cooking with Biomass**

3d	Household Heating and Cooking with Biomass	Emission Factors (mg/TJ)				
		Air	Water	Land	Product	Residue ng/kg
	Classification					
5	Open-fire 3-stone stoves (virgin wood)					200
6	Simple stoves (virgin wood)	10	0		0	200

The resulting emission factors for PCDD/PCDF are relatively low and close to the ones proposed in the 2005 edition of the Toolkit. As for the PCDD/PCDF in ashes, the emission factors derived were lower than the existing ones.

As it is anticipated that the use of simple stoves to substitute open fire in developing countries will increase substantially over the next years, other biomass sources or new types of devices may be considered for further investigation.

## Derivation of emission factors

### Release to Air

Releases to air are the predominant vector for biomass combustion. The default emission factor for class 1 was derived from mean values reported between 2 and 50 µg TEQ/t of wood burned. The values of 2.4–4.7 µg TEQ/kg as reported in the Austrian study seems to be extraordinarily high. The values of 0.2–0.7 µg TEQ/t as reported in the German study seem to represent the lowest end of the spectrum. So does the Swiss value of 24 ng TEQ/GJ. It is important to note that the values reported for clean biomass combustion are consistently one order of magnitude below the values reported for the combustion of contaminated biomass such as treated and/or painted wood. Thus, an average value of 1.5 µg TEQ/t was chosen for clean biomass where as a value of around 25 µg TEQ/t was used for contaminated biomass. Based on an average heating value of 12–15 MJ/kg for wood, default emission factors of about 100 µg TEQ/TJ can be calculated for clean biomass and 1,500 µg TEQ/TJ for contaminated biomass (LUA 1997, IFEU 1998). LUA (1997) gave emission factors of 50 µg TEQ/t for slightly contaminated and 500 µg TEQ/t for highly PCP-treated wood, which would result in emission factors of 3,300 µg TEQ/TJ and 50,000 µg TEQ/TJ, respectively.

Emissions resulting from the use of straw as a fuel (class 3) are investigated in Hedman (2006) and Schleicher (2002). These references cover a range from 375 to 575 µg TEQ/TJ.



Information on charcoal fired stoves (class 4) is scarce. The proposed value of 100 µg TEQ/TJ has to be considered as an expert estimate based on Schleicher (2002).

New emission factors for classes 5 and 6 are based on Cardenas *et al.* (2011).

### **Release to Water**

No release to water is expected.

### **Release to Land**

No release to land is expected unless the combustion takes place directly on the soil. Due to a lack of data, no default emission factor could be derived.

### **Release in Products**

The process has no product, thus no release to product occurs.

### **Release in Residues**

PCDD/PCDF in the ash residue range from a few nanogram to several thousand ng TEQ/kg (or µg TEQ/t, respectively). Combustion of virgin wood will generate lower concentrations in the ash whereas treated wood results in higher concentrations. The mean concentrations determined by Wunderli *et al.* (1996) will be used in the Toolkit as a first estimate: they determined an average of 1,000 ng I-TEQ/kg of ash generated for contaminated wood and 10 ng I-TEQ/kg of ash generated for clean wood. For peat as a fuel, no TEQ-based results were found. However, a publication by Mehrag and Killkam (2003) found 60.6 ng PCDD/PCDF (tetra-through octachlorinated homologs) per kg of peat ash in a sample from the 19th century. Applying the emission factor of class 2 for peat ash is suggested. Utilization of this factor would not underestimate the release.

The new class 3 emission factor for straw fired stoves is derived from Launhardt (2000). This value refers to the range reported for combustion chamber ash (5-33 ng TEQ/kg). Concentrations in heat exchanger ash are typically higher. With regard to mixed ashes a value at the upper end of the range is proposed. New emission factors for residues are included in classes 5 and 6 based on Cardenas *et al.* (2011).

## Annex 34 Complementary information to source category 3e Household Heating and Cooking with Fossil Fuels

### Overview of recent revisions

Three new classes were added in this category:

- Coal/biomass co-fired stoves with waste, including domestic stoves using mixed solid fuels. In most cases this category applies to the co-firing of coal, biomass and waste. Nevertheless, co-firing of waste in residential appliances is an illegal practice in many countries.
- Peat fired stoves, including domestic stoves, ovens and boilers firing peat. The use of peat as a fuel in the residential sector is closely linked to its local availability.
- Coal/coke-fired simple stoves, including coal ore coke fired simple stoves for cooking with limited combustion control. The proposed dioxin emission factor for air is of 200 µg TEQ/TJ. High chlorine coal fired stoves may show significantly higher emissions (Air: 1,500 µg TEQ/TJ coal, Residue: 5,000 ng TEQ/kg ash).

### Derivation of emission factors

#### Release to Air

Releases to air are the predominant vector for fossil fuel combustion. For coal, three classes of emission factors are proposed since there are distinct ranges of PCDD/PCDF emissions reported in the literature. The default emission factor for class 3 was derived from mean values reported between 1.6 and 50 µg TEQ/t of coal burned, which is reported from most European countries. It is important to note that the values reported for domestic coal combustion are fairly consistent between 1 and 7 µg TEQ/t of coal burned. Thus, an average value of 3 µg TEQ/t was chosen for typical coal. Based on an average heating value of 30 MJ/kg for coal, a default emission factor of about 100 µg TEQ/TJ can be calculated. On the other hand, an Austrian study reported a much higher value of 0.91 mg TEQ/t as well as the Swiss value of 230 ng TEQ/GJ also seems to be somewhat on the high side (LUA 1997). However, emission factors in the same range were recently reported for small residential stoves when coal or briquettes from Poland were burned resulting in an emission factor as high as 200 µg TEQ/TJ (Grochowalski and Konieczynski 2008). Kubica *et al.* (2004) reported emission factors between 108.5 µg TEQ/t and 663.9 µg I-TEQ/t of coal burned. These high values may be explained by the high chlorine content – ranges from traces to 0.4% and maxima up to 1.5% of chlorine - in the coal from Poland. For an average of 400 µg I-TEQ/t of coal burned and with an average heating value of 25 MJ/kg for bituminous coal from Poland (and coals from other regions with similar specifications), a class 1 default emission factor of 1,700 µg TEQ/TJ (Pandelova 2005). However, the role of chlorine concentration in the reaction gases from hard coal firing in combustion processes is not yet clearly explained. There are many processes inhibiting PCDD/PCDF formation as well. The NaCl content in coal seems to be less important in light of data obtained from recent measurements. These results indicate that even for 0,5 - 1% of NaCl (high chlorine coal) in coal fired in modern CFB boilers, PCDD/PCDF emissions are less than previously expected.

The new emission factor for peat fired stoves (class 4) was derived from McGettigan (2009).

The default emission factor for class 5 was derived from values reported between 0.04 and 2 µg TEQ/t. The value of 0.04 mg TEQ/t as reported in the Austrian study seems to be extraordinarily high whereas the Swiss value of 0.5 ng TEQ/GJ is extremely low. Thus, an average value of 0.5 µg TEQ/t was chosen for oil. Based on an average heating value of 44–46 MJ/kg for heating oil, a default emission factor of 10 µg TEQ/TJ was calculated.

The default emission factor for class 6 was derived from values reported between 0.04 and 0.07 ng TEQ/m<sup>3</sup>. An average value of 0.05 ng TEQ/m<sup>3</sup> was chosen for natural gas. Based on an average heating value of 32–35 MJ/m<sup>3</sup> for natural gas, a default emission factor of 1.5 µg TEQ/TJ was calculated (LUA 1997, IFEU 1998, Environment Canada 1999).

### **Release to Water**

No release to water is expected.

### **Release to Land**

No release to land is expected.

### **Release in Products**

The process has no product, thus no release to product occurs.

### **Release in Residues**

PCDD/PCDF in the fly ash residue of coal combustion has been analyzed and concentrations between 4 and 42,000 ng TEQ/kg ash were detected (Dumler-Gradl *et al.* 1995). For a first estimate, an emission factor of 5,000 ng TEQ/kg ash should be used in the Toolkit. For the high chlorine coal from Poland, no emission factor was found. However, for a first approximation the upper values of the measured data from Dumler-Gradl *et al.* (1995) could be used for class 1 residues.

## Annex 35 Complementary information to source category 4a Cement Production

### Overview of recent revisions

The emission factors for this source category have not been revised or otherwise changed. Additional guidance has been introduced on classifying sources within this category, estimating activity rates, and on data quality aspects.

### Derivation of emission factors

#### Release to Air

Emissions to air in terms of PCDD/PCDF produced per unit production will be influenced by the concentration of the PCDD/PCDF in the flue gas and the amount of gas produced per unit production. A larger volume of flue gas is generated in wet kilns per unit output than in dry kilns. Modern kilns produce between 1,500 and 2,500 m<sup>3</sup> per ton of clinker (BREF 2010).

The SINTEF study is based on more than 1,700 PCDD/PCDF measurements from the early 1990s until recently. It summarizes emissions to air from wet and dry kilns and from plants operating on fossil fuels and “natural” raw materials and plants utilizing alternative raw materials and alternative fuels. These alternative fuels and raw materials, including wastes, were co-fired to the main burner, to the rotary kiln inlet or the preheater/precalciner. In many countries, this is usual practice. The vast majority of the data reported have PCDD/PCDF concentrations far below 0.1 ng TEQ/m<sup>3</sup>; emissions from dry kilns may be slightly lower than those from wet kilns. Emissions in this range correspond to emission factors below 0.05 µg TEQ/t of cement. These plants were considered BAT and the emission factor represents class 4. However, the SINTEF study also includes some old data – from U.S.A. – which had an emission of up to 25.8 ng TEQ/m<sup>3</sup>, which corresponds to an emission factor of 16.7 µg TEQ/t of cement (SINTEF 2006).

Very low concentrations of PCDD/PCDF were found in the sampling campaign in Thailand at a cement plant utilizing the dry process. During normal operation (lignite/petroleum coke and full load), the stack emissions were all below 0.02 ng TEQ/Nm<sup>3</sup> and as low as 0.0001 ng TEQ/Nm<sup>3</sup>; the means were 0.0105 ng TEQ/m<sup>3</sup> and 0.0008 ng TEQ/m<sup>3</sup> for the normal operation conditions and 0.003 ng TEQ/Nm<sup>3</sup> and 0.0002 ng TEQ/Nm<sup>3</sup> for the tests performed with substitute secondary fuels, respectively. The resulting emission factors were at a mean 0.02 and 0.001 µg TEQ/t of clinker for the normal operation and 0.005 and 0.003 µg TEQ/t of clinker in the case of co-firing alternative fuels/wastes. Thus, all test results were far below the orientation value of 0.1 ng TEQ/Nm<sup>3</sup>. The results demonstrated that the addition of tires and/or liquid hazardous waste had no effect on the emission results keeping in mind that the dry cement kiln process employed in the cement plant is state-of-the-art technology and the plant is well-managed (UNEP 2001, Fiedler *et al.* 2002).

Concentration of PCDD/PCDF in the flue gases seems to be influenced by the temperature of the dust collection device. Low temperatures (<200°C) seem to indicate that typical concentrations will be under 0.1 ng TEQ/Nm<sup>3</sup>, temperatures over 300°C increase the likelihood of finding higher emissions, typical concentrations would be 0.3 ng TEQ/Nm<sup>3</sup> and above. In some cases much higher emissions may be

found. These seem to be linked to high dust collector temperatures, high levels of organic matter in the raw materials and may be linked to use of certain wastes under inappropriate conditions.

For the purpose of this Toolkit, an average emission factor of 5 µg TEQ/t of cement is applied for old kilns and with dust collectors operating at temperatures above 300°C (derived from old US data) for class 2. An average emission factor of 0.6 µg TEQ/t of cement is applied where the dust collector is between 200 and 300°C (class 3). An emission factor of 0.05 µg TEQ/t of cement is applied for modern plants where dust collector temperature is held below 200°C (class 4). Since there are no measured PCDD/PCDF data available for shaft kilns, no emission factor could be calculated and provisionally, class 1 has been incorporated for this technology and the same emission factor assigned as for the old wet kilns.

### **Release to Water**

Releases to water are not expected. However, if effluents are identified these should be noted and the origin in the process described.

### **Release to Land**

Some residues may be spread on land, in some cases the use of cement kiln dust to increase alkalinity and add lime has been reported. Any use of cement kiln dust (CKD) in this manner should be noted.

### **Release in Products**

Releases in the cement product are expected to be small since the product has been exposed to very high temperatures.

### **Release in Residues**

It should be mentioned that the dusts collected in air pollution control systems, typically electrostatic precipitators (ESP) or cyclones, mainly consist of raw materials fed into the kiln (at the end of the secondary burner). The remainder of the dust consists of emissions from the kiln that has passed the hot zone. Typically, the dusts from the ESPs/cyclones or bagfilters are re-introduced into the kiln.

In cases where solid residues from flue gas cleaning equipment are not recycled into the kiln, an initial estimate of release of PCDD/PCDF in CKD would be based on the assumption that approximately 30 kg of CKD per ton of clinker (0.03% of clinker production) is generated. This value is based on a report that gave 0.4 million tons CKD from 13.5 million tons of clinker/cement production (Dyke *et al.* 1997).

Concentrations of PCDD/PCDF in the CKD are expected to vary and a range of concentrations from 0.001 to 30 ng TEQ/kg has been reported for UK kilns (Dyke *et al.* 1997), 1-40 ng TEQ/kg were summarized for German tests (SCEP 1994). SINTEF (2006) and BREF (2010) report an average value of 6.7 ng I-TEQ/kg CKD, from 90 samples taken from wet and long dry kilns, from clinker cooling, from by-pass and ESPs in dry suspension preheater kilns.

## **Annex 36 Complementary information to source category 4b Lime Production**

### **Overview of recent revisions**

No revisions of emission factors have been made. Additional guidance has been introduced on classifying sources within this category, estimating activity rates, and on data quality aspects.

### **Derivation of emission factors**

#### **Release to Air**

Emissions have been measured from a number of German kilns (SCEP 1994). An emission factor of 0.07 µg TEQ/t of lime produced is to be used where lime kilns are well controlled and fitted with dust abatement equipment (typically electrostatic precipitator or fabric filter).

However, individual plants found in Europe (3 kilns, 2 rotary kilns and 1 shaft kiln in Sweden in the years between 1989 and 1993) showed measured concentrations between 4.1 and 42 ng N-TEQ/Nm<sup>3</sup>. All measurements of high PCDD/PCDF emissions were explained either by the raw material and/or fuel content, or the less than optimum burning conditions, underlining the importance of controlling the kiln inputs and maintaining a stable kiln operation (BREF 2010). Considerably higher emissions were also quoted for limited tests (LUA 1997), and an emission factor of 10 µg TEQ/t of lime produced is to be applied where control of the kilns is limited and dust control is basic (cyclone) or absent.

Raw materials or fuels that contain chlorides may potentially cause the formation of PCDD/PCDF in the combustion process of the lime kiln. Data reported from Europe, obtained from seven kilns, of which four were rotary kilns and three were shaft kilns, showed PCDD/PCDF concentrations below 0.1 ng TEQ/Nm<sup>3</sup>. Measurements at two annular shaft kilns in Germany were all below 0.05 ng TEQ/Nm<sup>3</sup>. However, the scarcity of measurements means it cannot be ruled out that individual plants may be found in Europe and elsewhere, which may have a local impact (LUA 1997).

High concentrations of PCDD/PCDF have been measured at three kilns, 2 rotary kilns and one shaft kiln, in Sweden. The measurements made between 1989 and 1993 gave concentrations between 4.1 and 42 ng N-TEQ/Nm<sup>3</sup>. All measurements of high PCDD/PCDF concentration have been explained either by the raw material and/or fuel content, or the less than optimum burning conditions, underlining the importance of controlling the kiln inputs and maintaining a stable kiln operation (BREF 2010).

#### **Release to Water**

No release to water is expected. Any effluent identified should be recorded and its source in the process identified.

#### **Release to Land**

Lime product or gas cleaning residues may be used on land. No information was available on levels of PCDD/PCDF in these to allow an estimate to be made of releases to land.

#### **Release in Products**

No information was available on PCDD/PCDF in lime products. Levels are expected to be low due to the high temperatures used in processing.

#### **Release in Residues**

A residue in the form of dust from gas cleaning operations may arise although this may be reused in the process or may have a product value. No information was available on PCDD/PCDF in such dust.

## Annex 37 Complementary information to source category 4c Brick Production

### Overview of recent revisions

The results of an experimental programme in Kenya, South Africa and Mexico, including measurements of PCDD/PCDF, PCB and HCB emissions in Mexico were used to revise and amend emission factors to air, residues and products.

From the experiments in Mexico, PCDD/PCDF, PCB and HCB emission factors to air, products (bricks) and residues (ashes) are available for two types of fuels (wood and heavy oil or “Combustoleo”). The resulting air emission factors found in Mexico confirmed the 2 classes of emission factors for air. Emission factors for PCB and HCB were equally generated. Emission factors for PCDD/PCDF, PCB and HCB in ashes and bricks were also developed. Emissions of HCB and marker PCB were shown to be more fuel related than PCDD/PCDF.

**Table III.37.1 Dioxin like PCBs in WHO TEQ emission factors for source category 4c Brick Production**

4c	Brick Production Classification	Emission Factors (µg TEQ/t brick produced)				
		Air	Water	Land	Product	Residues*
1	No emission abatement in place and using contaminated fuels	0.015	-	NA	0.01 <sup>i</sup>	0.001 <sup>iii</sup>
2	No emission abatement in place and using non-contaminated fuels	0.001	-	NA	0.001 <sup>ii</sup>	0.0001 <sup>iv</sup>
	Emission abatement in place and using any kind of fuel.					
	No emission abatement in place but state of the art process control					

\* In countries with no waste management or no reuse of the residue for brick making, this often goes to Land

<sup>i</sup> Derived from field measurements at Mexican artisanal brick kilns using waste oil

<sup>ii</sup> Derived from coal and virgin wood fired brick kilns in Mexico, South Africa at industrial and artisanal scale

<sup>iii</sup> Derived from Mexican artisanal brick kilns fired with contaminated fuels

<sup>iv</sup> Derived from virgin wood and coal fired kilns in Mexico, South Africa and Kenya at industrial and artisanal scale

**Table III.37.2 HCB emission factors for source category 4c Brick Production**

4c	Brick Production Classification	Emission Factors (mg/t brick produced)				
		Air	Water	Land	Product	Residues*
1	No emission abatement in place and using contaminated fuels	225	-	NA	100 <sup>i</sup>	1 <sup>iii</sup>
2	No emission abatement in place and using	32	-	NA	20 <sup>ii</sup>	0.1 <sup>iv</sup>



	non-contaminated fuels					
	Emission abatement in place and using any kind of fuel.					
	No emission abatement in place but state of the art process control					

\* In countries with no waste management or no reuse of the residue for brick making this often goes to Land

<sup>i</sup> Derived from field measurements at Mexican artisanal brick kilns using waste oil

<sup>ii</sup> Derived from coal and virgin wood fired brick kilns in Mexico, South Africa at industrial and artisanal scale

<sup>iii</sup> Derived from Mexican artisanal brick kilns fired with contaminated fuels

<sup>iv</sup> Derived from virgin wood and coal fired kilns in Mexico, South Africa and Kenya at industrial and artisanal scale

The comparison of PCDD/PCDF, PCB and HCB levels in soil, ash and brick samples from Kenya and South Africa to the levels found in Mexico suggest that emission factors measured in Mexico fit the variety of installations and fuels used in developing countries and can be applied in general.

Finally, the existing classes were further refined to better reflect the specific processes and technologies used in developing countries. Consequently, class 2 was amended to include technologies with no emission abatement in place and using non-contaminated fuels, using emission abatement and any kind of fuel, and with no emission abatement in place but state of the art process control.

Some hotspot situations were encountered during the field study. Significantly high levels of PCDD/PCDF were detected in ash and bricks of some Mexican sites co-incinerating waste, and indicate the need to assess further whether these data represent another category. Furthermore, typical Asian kiln types could not be included in this study, and further work should be done to include information on these types of kilns as well.

As it is anticipated that brick making will increase in developing countries, opportunities exist for South-South exchange of technologies and BAT/BEP in order to further reduce emissions.

## Derivation of emission factors

### Release to Air

An emission factor of 0.02 µg TEQ/t of product is to be applied to brick making processes with good control, consistently high temperatures and controls over the fuels used. Higher emissions may occur if poor controls are in place and wastes or poor quality fuels burned; then class 1 should be applied. These emission factors have been confirmed by studies in Mexico, South Africa and Kenya (Umlauf *et al.* 2011).

### Release to Water

No release to water is expected. Any effluent should be noted and its source recorded.

### Release to Land

No release to land is expected.

### **Release in Products**

Few data were available on levels of PCDD/PCDF in bricks, usually at or below the detection limit. The levels are generally expected to be low as the bricks have been subject to high temperatures. In one occasion in Mexico levels around 10 ng/kg TEQ were detected. However, it is assumed that most of the PCDD/PCDFs are immobilized within the bricks and should not be considered as an exposure relevant emission.

### **Release in Residues**

PCDD/PCDF may be present in residues from the process. Apart from one exception with levels around 100 ng/kg TEQ, the concentrations were usually in the low ng/kg TEQ range or non detected. Since the ash production is in the range of some kg per ton of bricks, this release pathway is generally negligible (Umlauf *et al.* 2011).

## **Annex 38 Complementary information to source category 4d Glass Production**

### **Overview of recent revisions**

No revisions of emission factors have been made. Additional guidance has been introduced on classifying sources within this category, estimating activity rates, and on data quality aspects.

### **Derivation of emission factors**

#### **Release to Air**

Tests in Germany on three glass producing furnaces showed low concentrations of PCDD/PCDF (SCEP 1994). The plants tested were fitted with dry sorption or wet scrubbing or electrostatic precipitators. Emissions factors for two plants were 0.005 and 0.022 µg TEQ/t of product, for the third plant concentrations were about a factor of 8 higher but an emission factor could not be calculated.

An emission factor of 0.015 µg TEQ/t of product should be applied to plants with pollution control systems and careful control over combustion conditions and material inputs to the kiln. An emission factor of 0.2 µg TEQ/t of product should be used where no gas cleaning is used and controls on plants may be less stringent.

#### **Release to Water**

Releases to water may occur where wet scrubbers are used. There is not enough information to estimate an emission factor in this case. The presence and source of effluents should be noted.

#### **Release to Land**

No release to land is expected.

#### **Release in Products**

Releases of PCDD/PCDF into glass products are expected to be very low due to the high processing temperatures.

#### **Release in Residues**

PCDD/PCDF may be present in residues from gas cleaning systems used in glass manufacture. No information was available to estimate an emission factor.

## **Annex 39 Complementary information to source category 4f Asphalt Mixing**

### **Overview of recent revisions**

No revisions of emission factors have been made. Additional guidance has been introduced on classifying sources within this category, estimating activity rates, and on data quality aspects.

### **Derivation of emission factors**

#### **Release to Air**

Tests have been carried out on asphalt mixing installations in Germany (SCEP 1994) and the Netherlands (Bremmer *et al.* 1994). The plants tested had fabric filters and some used cyclones as a pre-separator for dust. An average emission factor of 0.007 µg TEQ/t of product is to be applied to plants with this type of gas cleaning.

For plants without fabric filters an emission factor of 0.07 µg TEQ/t of product is applied (assuming fabric filters would capture approximately 90% of PCDD/PCDF).

Emissions may be highly increased where contaminated materials are used as part of the asphalt – for example fly ash from an old incinerator could lead to increased releases. Any incidence where such materials are used should be noted.

#### **Release to Water**

No release to water is expected. If effluents are released, their source in the process should be noted.

#### **Release to Land**

It is assumed that the asphalt is used on land but no data are available on the levels of PCDD/PCDF in it.

#### **Release in Products**

There may be PCDD/PCDF in the asphalt although levels are unknown. It is expected this will be used on land for road construction.

#### **Release in Residues**

Flue gas cleaning residues are likely to have PCDD/PCDF in them. Amounts are unknown. An initial estimate can be made by assuming that 90% capture of the PCDD/PCDF in the flue gas is achieved and assuming that the raw gas contains the same amount as for processes, which are uncontrolled giving an emission factor of 0.06 µg TEQ/t.

## **Annex 40 Complementary information to source category 4g Oil Shale Processing**

### **Overview of recent revisions**

No revisions of emission factors have been made. Additional guidance has been introduced on classifying sources within this category, estimating activity rates, and on data quality aspects.

### **Derivation of emission factors**

#### **Release to Air**

From an Estonian plant, two sets of emission data were reported – 0.40-4.8 pg TEQ/m<sup>3</sup> (at 6% O<sub>2</sub>) and 0.23-4.2 pg TEQ/m<sup>3</sup> (at 6% O<sub>2</sub>). The corresponding emission factors were calculated to be from 0.2 to 3.5 ng TEQ/t of oil shale. For the purpose of this Toolkit, a preliminary emission factor of 0.003 µg TEQ/t oil shale was chosen (Schleicher *et al.* 2004b).

According to Schleicher *et al.* (2004b), incoming oil shale is heated with hot flue gas, separated in cyclones and mixed with hot ash to attain the reaction temperature of at least 480°C. Kerogen is fractionated into gas, condensable oil, and a solid residue. The decomposition of the kerogen starts at around 300°C and proceeds more rapidly at higher temperatures (480-520°C). The vapor phase is cooled to result in an oil fraction and a gaseous phase. The gas is typically burned in a power plant and the oil fraction is further fractionated into heavy oil, light oil, diesel, and gasoline. A substantial part of the oil is used to heat up the Estonian power plant. The solid residue is subsequently burned with excess air in a special furnace at 750-800°C.

#### **Release to Water**

No release to water is expected. If effluents are released, their source in the process should be noted.

#### **Release to Land**

No release to land is expected. All solids are covered in the section on Release in Residues.

#### **Release in Products**

Estonia has analyzed two samples of oil shale that was mined in the northeastern part of this country and pyrolyzed to fuel. The concentrations measured in these oil shale samples were 0.61 and 0.75 ng TEQ/kg shale oil (Roots 2001).

#### **Release in Residues**

Schleicher *et al.* (2004b) report PCDD/PCDF concentrations between 1.9 and 2.9 ng TEQ/kg ash. An emission factor based on tons of oil shale produced cannot be calculated and thus, the annual release has to be calculated by using the mass of solid residues from all plants to be multiplied by the concentration in ash.

## Annex 41 Complementary information to source category 5a 4-Stroke Engines

### Overview of recent revisions

New information on emission factors for air releases was assessed and a revised emission factor is included for gasoline-powered vehicles with catalyst. Studies by several authors (Hagenmaier *et al.* 1990, Oehme *et al.* 1991, Abrantes *et al.* 2011) have shown that the emission factor for gasoline cars equipped with catalyst is not null, as suggested previously. Although the emission factor for this class is very small, a high number of these vehicles is in use worldwide.

Further, a new class 'ethanol fuel (with catalyst)' was introduced. Abrantes *et al.* (2011) showed that ethanol powered vehicles have lower emissions than gasoline powered vehicles. Thus an emission factor for ethanol vehicles equipped with catalyst is also considered.

### Derivation of emission factors

#### Release to Air

The annual average mileage, type and level of maintenance of vehicles are different worldwide. The use of leaded fuels decreased dramatically in Europe, Japan, and North America as a result of legislation; however, leaded fuel is still used in some other countries. Phase-out of leaded gasoline and adoption of catalytic converters as required in the EU Guideline 94/12/EG or similar legislation means that 4-stroke gasoline engines will become an almost negligible source of PCDD/PCDF emissions to air.

The emission factors listed in the Toolkit are based on studies in Germany and Belgium. Other countries, like North America and Asia, have very limited data on vehicle emissions.

Recent work on gasohol (gasoline with 22% ethanol) and ethanol powered vehicles, with a three-way catalyst in good working conditions, showed PCDD/PCDF releases of  $0.39 \cdot 10^{-3}$  and  $0.25 \cdot 10^{-3}$   $\mu\text{g TEQ/t}$  of fuel burned, respectively for gasohol and ethanol vehicles (Abrantes *et al.* 2011). The average results obtained by Abrantes *et al.* (2011), Hagenmaier (1990) and Oehme *et al.* (1991) are of  $0.00075 \mu\text{g TEQ/t}$  of fuel burned. Thus, an emission factor to air of  $0.001 \mu\text{g TEQ/t}$  of fuel burned is specified for class 3. Based on these results, an emission factor for ethanol- powered vehicles of  $0.0007 \mu\text{g TEQ/t}$  of fuel burned is equally included for class 4.

## **Annex 42 Complementary information to source category 5b 2-Stroke Engines**

### **Overview of recent revisions**

No revisions to emission factors in this source category have been made. Additional guidance has been introduced on classifying sources within this category, estimating activity rates, and on data quality aspects.

### **Derivation of emission factors**

#### **Release to Air**

Different emissions occur during different phases like start-up and engine warming. Since 2-stroke engines are mostly used for smaller engines, catalytic converters are hardly ever used.

The annual average mileage, type and level of maintenance of vehicles are different for different countries. In many cases, small engines are not very well maintained. This may result in higher emissions of PCDD/PCDF. Unfortunately, no data is available which relates the age and level of maintenance to the level of PCDD/PCDF emissions. All data used for deriving emission factors are based on various European studies.

## Annex 43 Complementary information to source category 5c Diesel Engines

### Overview of recent revisions

A new class, Biodiesel vehicles, was introduced in this source category. Additional guidance has been included on classifying sources within this category, estimating activity rates, and on data quality aspects.

### Derivation of emission factors

#### Release to Air

Limited data are available to evaluate PCDD/PCDF emissions from Diesel-fueled vehicles. So far, only passenger cars and trucks have been assessed; there are no data for off-road diesel uses (*i.e.*, construction vehicles, farm vehicles, and stationary equipment). From USA, there are two tailpipe studies where the Californian Air Resources Board reported a relatively high emission factor of 676 pg TEQ/km, corresponding to 3.2 µg TEQ/t of Diesel (assuming a consumption of 1 L Diesel for a 5.5 km distance driven; CARB 1987). Another study tested heavy-duty trucks and determined a range of emission factors from 3.0 to 96.8 pg TEQ/km (mean of 29.0 pg TEQ/km), corresponding to 0.014-0.453 µg TEQ/t of Diesel with a mean of 0.14 µg TEQ/t of Diesel (Gullett and Ryan 1997).

Schwind *et al.* (1991) and Hutzinger *et al.* (1992) reported emission factors between 32 and 81 pg TEQ/L (or 6-15 pg TEQ/km assuming a fuel consumption of 5.5 km/L) for a truck engine run under various simulated driving conditions. Hagenmaier *et al.* (1995) reported no emissions from a bus at a detection limit of 1 pg/L of fuel consumed for individual congeners. For diesel-fueled cars, Hagenmaier *et al.* (1990) reported an emission factor of 24 pg TEQ/L for one tested car.

Kim *et al.* (2003) investigated PCDD/PCDF emissions from diesel engines in US D-13 mode at load rates between 25% and 75% at constant speed (2,400 rpm). The mass concentrations for the three different loads of 14.4, 6.9, and 6.4 pg TEQ/m<sup>3</sup> convert into the following emissions factors: 2.0, 0.6, and 0.5 pg TEQ/L diesel (corresponding to 0.002 and 0.001 g TEQ/t of Diesel), which are lower than those reported in the studies by CARB, USEPA and the German universities (CARB 1987, Gullett and Ryan 1997, Schwind *et al.* 1991, Hutzinger *et al.* 1992).

More recently, Laroo *et al.* (2011) have tested modern diesel engines with catalyzed after-treatment and found PCDD/PCDF emissions from 0,21pg TEQ/L (0,51 pg TEQ/L for the 95% confidence interval) to 1,28 pg TEQ/L (2,89 pg TEQ/L for the 95% confidence interval), for the 2007 and 2010 emission control configurations respectively. From the above studies, an emission factor for Diesel-fueled vehicles of 0.1 µg TEQ/t of Diesel will be applied. If efficient soot filters are employed, emissions from consumption of Diesel fuel are much lower; currently, only a small proportion of vehicles in use are equipped with this technology.

Lin *et al.* (2011) have also tested a 1994 Diesel engine with premium diesel fuel (PDF) and several palm-biodiesel-PDF mixtures. The results showed PCDD/PCDF emissions of 1.43 ng TEQ/L, corresponding to 1.7 µg TEQ/t of premium diesel fuel, and 0.904 n TEQ/L, corresponding to 1.08 µg TEQ/t of B20 fuel



(20% palm-biodiesel and 80% diesel fuel). A new class and an emission factor of 0.07 µg TEQ/t (70% of regular diesel EF) are thus included for diesel fuel with at least 20% biodiesel.

### **Release in Residues**

Particulate emissions from Diesel engines are likely to contain PCDD/PCDF. Amounts are unknown, thus, more research is needed to determine actual PCDD/PCDF concentrations.

## Annex 44 Complementary information to source category 5d Heavy Oil Fired Engines

### Overview of recent revisions

The emission factor for heavy oil fired engines has been revised based on recent data. Cooper (2005) found an emission value of 0.5 µg TEQ/t of fuel burned, based on measurements on three ships, using marine gas oil or residual oil. Based on an array of studies, the revised emission factor value for this class is of 2 µg TEQ/t of fuel burned. Emission factors for other unintentional POPs (HCB and PCB) were also derived based on Cooper (2005) and are listed below.

**Table III.44.1 PCB emission factors for source category 5d Heavy Oil Fired Engines**

5d	Heavy Oil Fired Engines	Emission factors - µg TEQ/t of fuel burned				
		Air	Water	Land	Product	Residue
1	All types	550	NA	NA	NA	ND

**Table III.44.2 HCB emission factors for source category 5d Heavy Oil Fired Engines**

5d	Heavy Oil Fired Engines	Emission Factors (µg/t fuel burned)				
		Air	Water	Land	Product	Residue
1	All types	140	NA	NA	NA	ND

### Derivation of emission factors

#### Release to Air

Heavy oil fired engines cause PCDD/PCDF emissions to air. Unfortunately, limited data are available from isolated measurements in Europe and North America. Typically values between 3 and 6 µg TEQ per ton of fuel are reported from studies in Canada, the Netherlands, Sweden, and the US.

Measured data from the burning of recycled waste oils are available from Austria, where emissions from a small incinerator gave a concentration of 0.02 ng TEQ/Nm<sup>3</sup> (at 11% O<sub>2</sub>) equivalent to an emission factor of 0.37 µg TEQ/t of waste oil burned (LUA 1997). Dutch data from two small firing installations and a ferry determined a minimum of 0.1 ng TEQ/m<sup>3</sup> and a maximum of 0.3 ng TEQ/m<sup>3</sup> equivalent to emission factors of 2 µg TEQ/t and 6.5 µg TEQ/t, respectively. The mean of the measurements was 0.2 ng TEQ/m<sup>3</sup> (= 4.25 µg TEQ/t) and the median was 0.17 ng TEQ/m<sup>3</sup> (= 2.9 µg TEQ/t) (LUA 1997). Cooper (2005) has measured PCDD/PCDF emission from heavy oil and distillate maritime oil in diesel engines used on ships. The results showed emissions of 0.5 µg-TEQ/t (WHO-TEQ) for heavy oil burning. Based on these data, an emission factor of 2 µg TEQ/t of oil burned is determined.

Cooper (2005) has also measured emissions of HCB and PCBs from heavy oil and distillate maritime oil burning in diesel engines used on ships. Results were of 138,34 µg/t for HCB and 553,4 µg TEQ/t for total PCBs. Based on these data an HCB emission factor of 140 µg/t of heavy oil burned is proposed, and 550 µg TEQ/t of heavy oil burned for PCB.

#### Release in Residues

Heavy oil fired engines residues, especially emitted soot, are likely to have PCDD/PCDF in them. Unfortunately, amounts are unknown and further research is needed in order to determine exact concentrations.

## Annex 45 Complementary information to source category 6a Biomass Burning

### Overview of recent revisions

Since the last edition of the Toolkit (2<sup>nd</sup> version from 2005), new information has become available from several projects that have been implemented to provide emission factors for the open burning of different types of biomass. Especially one project commissioned by the Secretariat of the Stockholm Convention and implemented by UNEP Chemicals Branch improved the measurement techniques by running the same samples in open burn hut and field sampling methods; *i.e.*, the US-EPA Open Burn-hut Facility and the Australian “whoozle” technique by EnTox and CSIRO (Black *et al.* 2011a, UNEP 2011b). The same project also assessed all measured data and recommended an improved classification scheme and new emission factors for PCDD/PCDF. Suggested improvements included a new emission class, sugarcane burning, and substantial revisions to emission factors to land (Black *et al.* 2011b). Because better simulations or even field studies are available now, the older references have been removed from this section and replaced by the more recent studies. The revised emission factors for PCDD/PCDF are presented in Table II.6.3 and emission factors for dioxin-like PCB are given below:

**Table III.45.1 Dioxin-like PCB emission factors for source category 6a Biomass Burning**

6a	Biomass burning	Emission Factors (µg TEQ/t biomass burned)				
		Air	Water	Land	Product	Residue
	<b>Classification</b>					
1	Agricultural residue burning in the field, impacted poor burning conditions	3*		0.3*		
2	Agricultural residue burning in the field, not impacted	0.05		0.01		
3	Sugarcane burning	0.05		0.01		
4	Forest fires	0.1		0.1		
5	Grassland and savannah fires	0.03		0.03		

\* Based on expert judgment and analogy to PCDD/PCDF data

### Derivation of emission factors

PCDD/PCDF formation and release from open burning of biomass vary considerably depending on the biomass itself and the conditions under which it is burned, e.g., the nature and composition of the forest, grassland, savannah, crop or residue, moisture content, the presence of contaminants, such as pesticides or salt water residues.

Due the lack of containment of ashes from open burning of biomass, the  $EF_{Land}$  is given rather than  $EF_{Residue}$ , since the ashes are most often left on land or incorporated into the soil.

### Release to Air

For class 1 and 2, Gullett et al. (2002) performed biomass burns in a steel barrel in an open burn simulation facility and determined emission factors for wheat straw (containing ~0.8% Cl for spring straw and 0.08% for winter straw), rice straw (containing 0.33% Cl), and stubble (0.33% Cl). The wheat

straw  $EF_{Air}$  ranged from 0.337 to 0.602  $\mu\text{g TEQ/t}$  of straw burned and, the  $EF_{Air}$  for rice straw was 0.537  $\mu\text{g TEQ/t}$  of straw. In this study, as well as in a more detailed description given by Gullett and Touati (2003a), an  $EF_{Air}$  of 0.5 ng TEQ/kg was regarded as appropriate for both residues. The authors specified that the spring wheat had been treated with non-chlorinated herbicides but gave no information on other residues.

For class 3, Meyer *et al.* (2004a, 2004b) reported an  $EF_{Air}$  of 0.8 ng TEQ/kg for burning sugarcane in fields in Australia, which was about three times less than the  $EF_{Air}$  determined in a facility intended to simulate open burning conditions. A laboratory burn facility was used to determine emission factors for sugarcane fires using sugarcane leaves and stalks (Gullett and Touati 2006) with mean PCDD/PCDF emission factors of 126  $\mu\text{g TEQ/t}$  of fuel (range 98-148  $\mu\text{g TEQ/t}$  of fuel) (Hawaii) and 12  $\mu\text{g TEQ/t}$  of fuel (range 5.5 -26  $\mu\text{g TEQ/t}$  of fuel) (Florida 1) and 5  $\mu\text{g TEQ/t}$  of fuel (range 0.13-1.72  $\mu\text{g TEQ/t}$  of fuel) (Florida 2).

For forest fires (class 4), Black *et al.* (2011a, 2011b) derived  $EF_{Air}$  for forest fuel (Duke Forest, North Carolina) of 0.52 (range: 0.40–0.79), 0.59 (range: 0.18–1.2) and 0.75 (range: 0.27–1.2)  $\mu\text{g TEQ/t}$  of fuel consumed for the in-field, over a brick hearth, and burn facility experiments, respectively. In Australia, an  $EF_{Air}$  of 0.5 ng TEQ/kg was derived for forest fires (wildfires and prescribed burns) and an  $EF_{Air}$  of 1.0 ng TEQ/kg for savannah fires (class 5). This project entailed measurements of PCDD/PCDF air emissions from 21 field burns and 19 laboratory tests (Meyer *et al.* 2004a; Meyer *et al.* 2004b).

Forest fire simulations in a laboratory burn facility were used to estimate PCDD/PCDF emission factors of 19  $\mu\text{g TEQ/t}$  of fuel (range 1-56  $\mu\text{g TEQ/t}$  of fuel) for biomass from Oregon and North Carolina (Gullett and Touati 2003b). Further forest fire simulations (Gullett *et al.* 2008) produced PCDD/PCDF emission factors ranging from 0.15  $\mu\text{g TEQ/t}$  of fuel to 13  $\mu\text{g TEQ/t}$  of fuel from forest biomass collected from four regions in North Carolina.

### Release to Water

No  $EF_{Water}$  is given since no direct release to water is expected. It should be noted that rainfall may wash away ash particles and some of this may enter water courses with relevance to subsequent contamination of receiving waters including sediments.

### Release to Land

PCDD/PCDF are expected to be present in residues, which may be left on land or incorporated into the field surface constituting a release to land. PCDD/PCDF may be expected to be present in the ashes from fires. In some cases, these ashes may be used for their mineral content in agriculture. Ash production from these fires will vary with the conditions and the nature of the material combusted.

For class 1 and 2, Zhang *et al.* (2011) derived an  $EF_{Land}$  of 0.20 ng TEQ/kg for pesticide-contaminated corn straw and an  $EF_{Land}$  of only 0.002 ng TEQ/kg for uncontaminated corn straw. The finding by Walsh (1994) of no increase in PCDD/PCDF concentrations in soil following controlled straw field burning tests in the United Kingdom suggests that PCDD/PCDF concentrations in the ash were very low. Support for a low  $EF_{Land}$  for burning non-impacted agricultural residues can be drawn from the findings of studies related

to forest fires. For example, results from experimental burning of leaf litter and soil by Prange *et al.* (2003) indicate that releases to air are far greater than releases in ash and soil.

For class 3, using a portable field sampler to measure PCDD/PCDF emissions from open burning of sugarcane, a brick hearth to eliminate potential soil effects, and a laboratory burn facility, Black *et al.* (2011a) derived  $EF_{Air}$  of 1.1 (range: 0.40–2.2), 1.5 (range: 0.84–2.2) and 1.7 (range: 0.34–4.4)  $\mu\text{g TEQ/t}$  fuel consumed for in-field, over a brick hearth, open field and burn facility experiments respectively.

Gullett *et al.* (2006) reported that simulated pre-harvest burning of sugarcane produced about 4% ash that had PCDD/PCDF concentrations of 0.004 to 1.22 ng TEQ/kg  $C_{Initial}$ .

For forest, grassland and savannah fires, two previous studies and the current work provide data from which emission to land can be estimated. The average ash concentration of 1.1 ng TEQ/kg ash when combined with the appropriate burning efficiency yields emission factors to land of 0.05  $\mu\text{g TEQ/t}$  for sugar cane and 0.15  $\mu\text{g TEQ/t}$  fuel burned, which is more than 20-fold lower than the 2005 Toolkit emission factors.

### **Release in Products**

No  $EF_{Product}$  is provided. No product is expected.

### **Release in Residues**

No  $EF_{Residue}$  is provided since residues are typically left in place so that any accompanying releases are assumed to be to land.

## Annex 46 Complementary information to source category 6b Waste Burning and Accidental Fires

### Overview of recent revisions

Similarly to the section on biomass, since the 2<sup>nd</sup> edition of the Toolkit (2005) new information has become available for the open burning of waste from several projects that have been implemented to provide better emission factors and especially taking into consideration circumstances in developing countries. The projects included field experiments in Mexico and China that added a total of 30 results to improve the emission factors for dump fires (class 1) and burning of loosely arranged domestic waste (class 3) (Solorzano-Ochoa *et al.* 2012, Zhang *et al.* 2011, UNEP 2011a). Besides providing new emission factors, the characterization of the activity has also been made more specific and a protocol and a sampler for undertaking field sampling have been developed. Although the emission factors for PCDD/PCDF and dioxin-like PCB scatter across a large range between measurements, the confidence in these data is relatively high.

**Table III.46.1 Dioxin-like PCB emission factors for source category 6b Open Burning of Waste and Accidental Fires**

6b	Open Burning of Waste and Accidental Fires Classification	Emission Factors ( $\mu\text{g TEQ/t}$ material burned)				
		Air	Water	Land	Product	Residue
1	Fires at waste dumps (compacted, wet, high organic carbon content)	30				
2	Accidental fires in houses, factories					
3	Open burning of domestic waste	2				
4	Accidental fires in vehicles ( $\mu\text{g TEQ per vehicle}$ )					
5	Open burning of wood (construction/demolition)					

Although first, indicative measurements were undertaken for hexachlorobenzene and pentachlorobenzene, these emission factors are not proposed for inclusion into this Toolkit since the sampling resin (polyurethane foam) has not been adapted to these more volatile POPs and breakthrough or losses of analytes cannot be excluded. A literature study identified new information for class 4, accidental fires of cars that confirmed the present  $EF_{\text{Air}}$ . For order-of-magnitude assessments, the earlier  $EF_{\text{Air}}$  was changed to 100  $\mu\text{g TEQ per vehicle burned}$ .

### Derivation of emission factors

#### Release to Air

Open burning of mixed municipal solid waste is addressed in two classes within this sources category: 6b1 - Fires at waste dumps (compacted, wet, high organic carbon content) and 6b3 – Open burning of domestic waste. Both waste content and open burning of waste are highly variable and difficult to characterize. Emission factors for open burning of waste from the early Toolkit versions (1<sup>st</sup> and 2<sup>nd</sup>

edition of the UNEP Toolkit) were based on experiments from laboratory simulations (USEPA 1997, Gullett et al. 1999, Lemieux *et al.* 2003).

For open burning of domestic waste, Zhang et al. (2011) measured PCDD/PCDF releases to air from 20 field burns of urban, semi-urban and rural wastes in China and Mexico using a newly developed sampling system. In China, the contents of each type of waste were based on literature surveys and field observation of wastes. For the ten field burns in China, an average  $EF_{Air}$  of 18 ng TEQ/kg (range 3.0 to 51 ng TEQ/kg) was determined. In Mexico, waste compositions were based on results of sampling and analyzing materials at landfills in rural, semi-urban and urban-industrial areas of Mexico. For the ten field burns in Mexico, an average  $EF_{Air}$  of 20.4 ng TEQ/kg (range 35 to 650 ng TEQ/kg) was derived.

In Sweden, Hedman *et al.* (2005) burned garden waste and refuse derived fuel (“municipal waste where the combustible fractions (*e.g.* paper, textile and soft plastics) had been mechanically sorted out from noncombustible waste and decomposable material at a waste sorting plant”) in open steel barrels and on a steel plate. They reported air emission factors of 4-72 ng TEQ/kg, with a median value of 20 ng WHO-TEQ/kg. More specifically, Hedman (2005) reported  $EF_{Air}$  of 16-18 ng TEQ/kg.

For fires at landfills and waste dumps, a number of simulations and small scale studies have investigated varying waste composition, in particular chlorine and metal content to explain the variability in emission factors for PCDD/PCDF (*e.g.*, Ikeguchi and Tanaka 2000, Nakao *et al.* 2006, Gullett *et al.* 1999, 2001). They have not generated conclusive results and recent experiments at laboratory scale in burn huts showed that small scale experiments do not necessarily mimic field situations (UNEP 2010b). Therefore, for the determination of emission factors for open burning of waste at landfills and waste dumps in this Toolkit, only large scale, field experiments were further assessed.

Thirty recent field experiments were conducted in four campaigns (Solorzano Ochoa *et al.* 2011, Zhang *et al.* 2011), three in Mexico and one in China.  $EF_{Air}$  for PCDD/PCDF (in TEQ) spanned over three orders of magnitude, *i.e.*, ranged from 13  $\mu\text{g TEQ/t } C_{burned}$  to 14,000  $\mu\text{g TEQ/t } C_{burned}$ .<sup>20</sup> In one of the Mexican campaigns, although only six experiments were performed, extremes of conditions (stirred combustion to compacted, moistened, waste without stirring) were performed on the same waste composition. In these experiments, the  $EF_{Air}$  spanned over two orders of magnitude (from 290  $\mu\text{g TEQ/t } C_{burned}$  to 14,000  $\mu\text{g TEQ/t } C_{burned}$ ). The stirred experiments generated the lowest emission factors and the unstirred, compacted experiment with added water yielded the highest (Solorzano Ochoa *et al.* 2011, Zhang *et al.* 2011). Higher  $EF_{Air}$  are observed at higher ratios of CO/CO<sub>2</sub>; both occurred at later stages of the burning experiments when mass loss was lowest.

These experiments suggest that unattended, smoldering, poorly oxygenated open burning yields the highest emissions. Better combustion conditions, induced by stirring (presumably better oxygen supply and higher combustion temperatures), give rise to less-polluting open burning. Such conclusion is consistent with the recommendations that were provided in the BAT&BEP guidance document elaborated for the Stockholm Convention (UNEP 2007). This also means that only small piles could be stirred and large-scale open burnings of entire dumps may be analogous to the unstirred experiments.

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<sup>20</sup>  $C_{burned}$  is calculated from the carbon content of CO and CO<sub>2</sub> resulting from combustion and are assumed to comprise the totality of airborne carbon, with other forms negligible by comparison.



The results from the Mexican and Chinese field campaigns support the use of two distinct classes within the Toolkit source category 6b: compacted repositories vs. loosely arranged piles. Promoting good combustion conditions seems to be a solid and basic principle; however, considerable additional work should be done to fully understand the mechanistic factors that drive the emission factors towards the higher or lower end of the scale. These experiments also allowed derivation of  $EF_{Air}$  for dl-PCB whereas the sampling method was not optimized to securely derive  $EF_{Air}$  for the more volatile unintentional POPs, namely hexachlorobenzene (HCB) and pentachlorobenzene (PeCBz).

Since the last version of the Toolkit, no additional information was found for class 6b2 – Accidental fires in houses, factories. Materials burned and conditions experienced in accidental fires vary enormously. Limited data are available giving air emissions from such fires. Given the difficulties of measuring air emissions, most studies have used laboratory simulations or measured PCDD/PCDF in soot and residues. Some studies have considered air emissions from the burning of PVC only and provided air emission factors based on soot production in the range 40-3,500  $\mu\text{g TEQ/t}$  (based on summary by Carroll 1996). These factors were based on results from laboratory and real fire samples and assume that 20% of the PVC remains unburned and that all emissions to air are captured in the soot. Merk et al. (1995) burned wood and PVC in a closed room and measured levels of PCDD/PCDF in the air/flue gas in the room as well as in wipe samples from the walls. Assuming all the air in the room was contaminated at the levels measured an  $EF_{Air}$  of 560  $\mu\text{g TEQ/t}$  of PVC or 51  $\mu\text{g TEQ/t}$  of the wood/PVC mixture is obtained. Further it was assumed that deposited soot is additional to this a further 2,200  $\mu\text{g TEQ/t}$  PVC or 200  $\mu\text{g TEQ/t}$  PVC/wood mixture was produced. Ikeguchi and Tanaka (1999) provide air emission factors for the open burning of various wastes (220  $\mu\text{g TEQ/t}$  for scrap tires, 1,000  $\mu\text{g TEQ/t}$  for electric wire tube and 6,600  $\mu\text{g TEQ/t}$  for agricultural plastics (PVC)). Testing in Denmark of PCDD/PCDF released from burning chemicals (Vikelsøe and Johansen 2000) showed an enormous range of air emission factors (at 500°C) from 1  $\mu\text{g TEQ/t}$  for dichlobenil, up to 740,000  $\mu\text{g TEQ/t}$  for pentachlorophenol (PCP), and 100  $\mu\text{g TEQ/t}$  for PVC. At 900°C yields were greatly reduced. After a review of accidental fire data, air emission factors for residential fires of 83  $\mu\text{g TEQ/t}$  to air, 83  $\mu\text{g TEQ/t}$  in locally deposited soot and for industrial fires 500  $\mu\text{g TEQ/t}$  to air and 500  $\mu\text{g TEQ/t}$  in locally deposited soot were developed for Germany (LUA 1997).

Given the wide range of materials considered under accidental fires and the wide range of possible emission factors an initial estimate can be made by applying an  $EF_{Air}$  of 400  $\mu\text{g TEQ/t}$  to accidental fires.

Some new information was found for class 6b4 – Accidental fires in vehicles. Two studies were taken into account when deriving the emission factor for the release of PCDD/PCDF from fires in vehicles. Wichmann *et al.* (1995) carried out experiments in a tunnel with an old car (1974), a new car (1988), a subway car and a railway carriage. Emissions to air were estimated from PCDD/PCDF deposited inside the tunnel and no estimate was made of PCDD/PCDF, which may not have been deposited. Emissions were 32  $\mu\text{g TEQ}$  for the old car, 44  $\mu\text{g TEQ}$  for the new car, 2,000  $\mu\text{g TEQ}$  for the subway car and 9,200  $\mu\text{g TEQ}$  for the railway wagon. For the purposes of making an initial estimate a composite emission factor is developed assuming 49.5% of vehicle fires involve “old” cars, 49.5% involve new cars and 0.5% each of vehicles represented by subway cars and railway wagons giving a factor of 94  $\mu\text{g TEQ}$  per incident. Lönnermark and Blomqvist (2006) measured emissions from an automobile fire. Three separate full scale fire tests have been undertaken: a fire ignited and developed in the engine

compartment; a fire ignited inside the coupé, that was extinguished in the early stages; and a similar fire ignited inside the coupe´ that was allowed to spread until the entire vehicle was involved in the fire. The emissions to air were from 71.1 g I-TEQ per car to 86.8 g I-TEQ per vehicle. Combining the results from the Wichmann *et al.* (1995) and Lönnermark and Berqvist (2006), an  $EF_{Air}$  of 100 g per vehicle was assigned. This  $EF_{Air}$  is per incident not per ton of material.

No change was undertaken for class 6b5. It is relatively common to see fires used to dispose of wastes from construction and demolition – these are often predominantly burning wood but may also be used to dispose of other materials. Again little information is available either on the amounts burned or on emissions. When Wasson *et al.* (2005) burned aged and weathered chromated copper arsenate (CCA) treated wood was burned in USEPA’s burn hut, they reported PCDD/PCDF levels averaging 1.7 ng TEQ/kg of treated wood burned. Studies in Japan can be used to make an initial estimate of a suitable emissions factor to be applied – 60 µg TEQ/t (Ikeguchi and Tanaka 1999).

### Release to Water

There is little information available on the release of PCDD/PCDF to water from these types of fires. The releases will vary considerably but highest releases may result from the use of water to extinguish a fire or rain falling on a fire site and washing material into water courses. Since these processes will depend on local circumstances it is not possible to provide emissions factors but the issue may be important.

### Release to Land

Based on the recent experiments, an  $EF_{Land}$  (or  $EF_{Residue}$ ) as derived from the experiments by Lemieux *et al.* (2003) were revised as follows: for class 1, an  $EF_{Land}$  of 10 µg TEQ/t waste and for class 3 an  $EF_{Land}$  of 1 µg TEQ/t waste are proposed.

The  $EF_{Land}$  for classes 2, 4, and 5 remain unchanged. For accidental fires there is little information on levels of PCDD/PCDF in residues. A wide range of concentrations has been measured but there is often insufficient information to estimate an emission factor since the amounts of ash produced are not known. In Germany, an estimate was made that gave emission factors in residues (including deposited soot) of 1,000 µg TEQ/t for industrial fires and 350 µg TEQ/t for residential fires (LUA 1997). As an approximation and to make an initial estimate, an emission factor of 400 µg TEQ/t is used giving equal PCDD/PCDF in air emissions and in residues on average from the fires considered. For vehicle fires the limited testing in Germany (Wichmann *et al.* 1995) gave amounts of PCDD/PCDF left in residues, a composite emission factor is used to make an initial estimate – 18 µg TEQ per incident (using the same assumptions as above). Note, this emission factor is per incident not per unit mass. For fires involving construction and demolition wood, no emission factors were found. To make a preliminary estimate, an emission factor of 10 µg TEQ/t wood burned is suggested (from UK work on industrial wood combustion, Dyke *et al.* 1997). Note that treated wood, mixed fire loads and poor conditions may increase the amount of PCDD/PCDF in residues considerably.

### Release in Products

No  $EF_{Product}$  is provided. No product is expected.

### Release in Residues

No  $EF_{Residue}$  is provided. Residues are assumed to be releases to land since they are typically left in place.

### Detailed methodology

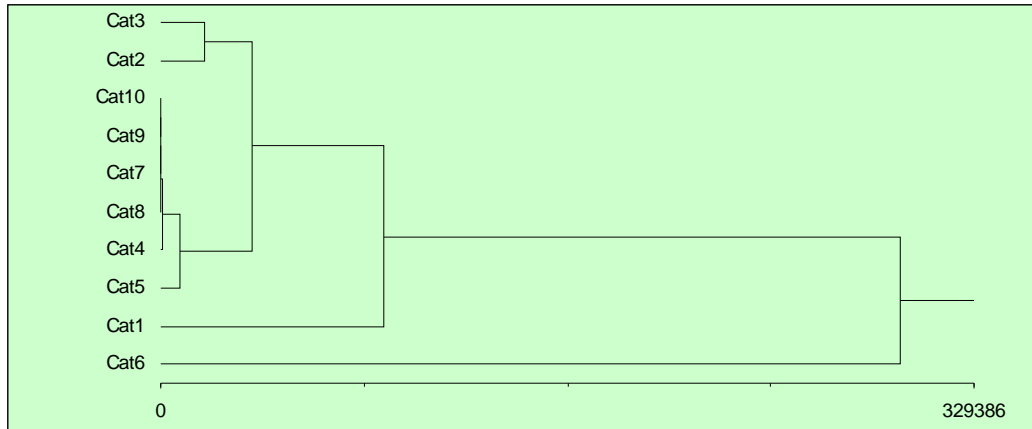
Emission factors to air were calculated as ng TEQ per kg of carbon burned (ng TEQ/kg  $C_{burned}$ ).  $C_{burned}$  is calculated from the carbon content of CO and CO<sub>2</sub> resulting from combustion and are assumed to comprise the totality of airborne carbon, with other forms negligible by comparison. Emission of PCDD/PCDF per ton of waste ( $\mu\text{g TEQ/t waste}$ ) is calculated by multiplying  $EF_{Air}$  (ng TEQ/kg  $C_{burned}$ ) by the carbon content of the waste and the experimental carbon oxidation factor (COF) (Fiedler *et al.* 2009).

A new practical approach has been developed to allow inventory developers to better characterize the activity, *i.e.*, estimate the mass of waste, which is burned in the open air. The new method takes the whole amount of waste present for the burn event into account. The new method is based on the fact that not all organic carbon that is present in the original waste will be burned; of the carbon burned, the majority is converted to carbon dioxide and carbon monoxide; a much smaller portion to PCDD/PCDF and other organic hydrocarbons. From experimental data, it was concluded that approximately only 40% by weight of the waste is combustible carbon. In line with global climate calculations of biomass combustion, a carbon oxidation factor of 58% was applied, meaning that only 58% of the 40% combustible carbon burns, resulting in an estimated 23% of the original carbon weight is actually combusted. When the carbon content in the waste is higher and better burn-out is obtained, the overall COF resulted in 42%. Applying the lower and the higher COF to the experimental set in Mexico, the  $EF_{Air}$  would be obtained (Table II.46.2).

**Table III.46.2 Derivation of  $EF_{Air}$  using two different COF**

$EF_{Air}$ (ng TEQ/kg $C_{burned}$ )	Conversion factor		Reference
	23%	42%	
823	189	346	Gullett et al. 2010
14,000	3,220	5,880	Solorzano Ochoa <i>et al.</i> 2011
660	152	277	Soloarzano Ochoa <i>et al.</i> 2011
290	67	122	Solorzano Ochoa <i>et al.</i> 2011
870	200	365	Solorzano Ochoa <i>et al.</i> 2011
950	219	399	Solorzano Ochoa <i>et al.</i> 2011
950	219	399	Solorzano Ochoa <i>et al.</i> 2011

An initial assessment of national release inventories made with the UNEP Toolkit has shown that open burning of biomass, such as forest, bush and grassland fires, burns in agriculture, and of waste are major sources of PCDD/PCDF in developing countries. Among the ten source groups, Source Group 6 Open burning contributes with an average of 61% to the total TEQ of all emissions to air; a second contributor is Source Group 1, mainly due to incineration of medical waste with approximately 12% and a third is Source Group 3 energy conversion and heating/cooking with approximately 7%. When PCDD/PCDF release inventories are compared, a hierarchical cluster analysis shows that Source Group 6, Open Burning, makes the difference between all inventories (Fiedler 2011).



**Figure III.46.1 Dendrogram of the ten source groups in the UNEP Toolkit applied to 60 PCDD/PCDF inventories demonstrating similarities and dissimilarities**

A total of 41 countries reported their releases of PCDD/PCDF – in g TEQ per year - to Air and Land for the open burning of biomass and waste (Table III.46.3, Fiedler 2011). The total releases were 18,363 g TEQ and reference year, whereby 8,958 g TEQ were emitted to air and 9,405 g TEQ to land. Considering the contribution from source categories 6a and 6b, 4,610 g TEQ were from biomass burnings and 13,753 g TEQ from waste burnings or accidents.

Noteworthy is that nine countries reported zero for releases from biomass (Guatemala, Pakistan, Tajikistan) or waste burnings (Bolivia, Cameroon, China, Honduras, Montenegro, Ukraine, Venezuela), respectively. Besides the difficulties to quantify the amount of material consumed in annual fires or doubts on the applicability of the emission factors, legal implications may be the driver for setting annual emissions to zero.

**Table III.46.3 Summary of descriptive statistics for the assessment of annual releases of PCDD/PCDF (expressed as g TEQ/yr) from open burning of biomass and waste**

Fuel	Biomass		Waste	
	Air	Land	Air	Land
Release Vector	Air	Land	Air	Land
Mean	24%	16%	32%	29%
Median	9%	5%	32%	34%
Std Dev.	29%	23%	28%	26%
Variance	8%	5%	8%	7%
25 <sup>th</sup> Percentile	1%	0%	1%	0%
75 <sup>th</sup> Percentile	56%	28%	48%	52%

## Annex 47 Complementary information to source category 7a Pulp and Paper Production

### Overview of revisions of emission factors

Emission factors for have been revised for power boilers in the pulp and paper industry as explained in the following section.

#### Release to Air

For pulp and paper mills, the major sources of PCDD/PCDF release to air are power boilers used to generate heat/power, rather than the pulp and paper production processes. Fuels burned in power boilers commonly include clean hog fuel (waste wood), salt-laden hog fuel (primarily at coastal and near-coastal mills), black liquor, wastewater treatment sludge, and de-inking sludge. However, clean hog fuel may also include other materials – wood product residues, plywood, agricultural wastes, paper, plastics, lubricating oils, municipal and industrial waste, rail ties, tires, etc. – that may impact PCDD/PCDF releases from power boilers (Uloth and van Heek 2002, Sinkkonen *et al.* 1997, Duo 2008).

Using data from Canadian pulp and paper mills, Uloth and van Heek (2002) derived the air emission factors shown in Table III.47.1:

**Table III.47.1 PCDD/PCDF Air Emission Factors for Power Boilers**

Type of boiler	Fuel	EF <sub>Air</sub> (µg TEQ/t dry fuel)
Power boilers	Clean hog fuel (with or without wastewater treatment sludge)	0.04
Power boilers	Clean hog fuel and de-inking sludge (with or without wastewater treatment sludge)	0.750
Power boilers	Black liquor	0.015
Kraft mill smelt dissolving tanks		0.00055
Sulfite process power boilers		0.0005

Based on Environment Canada (2002), the median and mean emissions from eleven U.S. kraft recovery furnaces were of 0.013 and 0.018 ng TEQ/kg black liquor solids (range:  $6.6 \times 10^{-5}$  to 0.0724), respectively, translating to an emission factor of 0.021 and 0.029 g/ADt pulp, respectively. Further, the median and mean emissions of PCDD/PCDFs from 15 pulp mill boilers from the US and Canada, firing 100% inland wood residues, were of 38.5 and 451.6 ng TEQ/bone dry ton hog fuel, respectively (range 3.3 to 2,799). This translates to a median and mean emission rate of 0.04 and 0.45 g TEQ/dry ton of wood combusted, respectively.

Other scientists, national agencies and trade associations have also derived air emission factors for power boilers burning black liquor, based on measurements at mills in their respective countries, as shown in Table III.47.2:

**Table III.47.2 PCDD/PCDF air emission factors for power boilers burning black liquor**

Agency/Association	EF <sub>Air</sub> (µg I-TEQ/t black liquor solids)
New Zealand Ministry of Environment (2011)	0.026, 0.036 and 0.014
Statistics Norway (2011)	1
NCASI (USEPA 2000; used by USEPA 2006)	0.07
Iwata <i>et al.</i> (2008) (Japan)	0.006/t pulp

In Japan, power boilers burning black liquor have an EF<sub>Air</sub> of 0.006 µg/t of pulp for PCDD/PCDF and dioxin-like PCBs, an EF<sub>Air</sub> of 2.4 µg/t for HCB and an EF<sub>Air</sub> 19.4 µg/t for PCBs (Ota *et al.* 2005).

### Release to Water

The pulp and paper industry is one of the largest industrial water users. If cooling water and other clean water are discharged separately, a bleached Kraft mill discharges water at a rate of 30-50 m<sup>3</sup>/ADt pulp and an unbleached Kraft mill has a water discharge rate of 15-25 m<sup>3</sup>/ADt pulp. For sulfite mills, water usage is about 70 m<sup>3</sup>/ADt pulp (EC 2001).

Concentrations in effluents ranged from 3 pg TEQ/L to 210 pg TEQ/L with a median of 73 pg TEQ/L (USEPA 1998). The default emission factor for Kraft bleached pulp using old bleaching sequences is 4.5 µg TEQ/t of pulp. Alternatively, the concentration in the effluent can be used and multiplied with the total mass of water discharged per year to calculate the annual release.

Data generated and published by NCASI (1998) in the USA from 20 bleach lines at 14 U.S. Kraft mills that use complete chlorine dioxide substitution for chlorine gave 119 data pairs for 2,3,7,8-Cl<sub>4</sub>DD and 2,3,7,8-Cl<sub>4</sub>DF in pulp mill effluents. The results showed that 2,3,7,8-Cl<sub>4</sub>DD was not detected in any sample above the proposed guideline concentration of 10 pg/L. 2,3,7,8-Cl<sub>4</sub>DF was detected in two samples from the acid stage at concentrations in the range of 15-18 pg/L and in the alkaline stage at concentrations in the range 11-18 pg/L.

The default emission factor for releases from modern wood pulp mills utilizing chlorine dioxide will be set to 60 ng TEQ/t of bleached pulp using a conservative approach. The emission factor will be applied only if there is direct discharge into the environment. If sludge is generated, the dioxin freight will be collected in the sludge and the effluents leaving from the effluent treatment plant will have non-accountable concentrations of PCDD/PCDF.

In China, a PCDD/PCDF concentration of 10.11 pg TEQ/L was measured in wastewater from an integrated bleached Kraft mill for cereal and rice straw (Zhang *et al.* 2001). At another Chinese pulp mill for reeds, a PCDD/PCDF concentration of 316 pg I-TEQ/L was measured in wastewater from bleaching processes (Zheng *et al.* 2000).

In Taiwan, PCDD/PCDF concentrations in raw wastewater of four pulp and paper mills ranged from 0.13 to 10.1 pg I-TEQ/L, with a mean of 5.1 pg I-TEQ/L, and, in the final treated effluent, PCDD/PCDF concentrations ranged from 0.06 to 0.51 pg I-TEQ/L, with a mean of 0.3 pg I-TEQ/L (Duh *et al.* 2007).

In mechanical pulp and paper mills (integrated mills, TMP), the water systems are usually quite closed in order to maintain high process temperatures. Consequently, wastewater volumes are small – 5-10 m<sup>3</sup>/ADt. No emission factors were found.

Pulping of pentachlorophenol treated wood may increase the concentrations in the effluent although no data have been published. Any use of PCP or of PCP-treated wood in the pulp and paper industry should be notified.

### Release in Products

Products from the pulp and paper industry can be contaminated with PCDD/PCDF, depending on the bleaching technology. High concentrations of PCDD/PCDF in pulp and paper products have been reported with the use of Cl<sub>2</sub> in bleaching processes. Replacing Cl<sub>2</sub> with chlorine dioxide (ClO<sub>2</sub>) – so-called elemental chlorine free (ECF bleaching) – may reduce 2,3,7,8-Cl<sub>4</sub>DD and 2,3,7,8-Cl<sub>4</sub>DF concentrations to non-detectable levels. However, ClO<sub>2</sub> commonly contains small amounts of Cl<sub>2</sub> so that PCDD/PCDF formation may still occur during ECF bleaching. The extent of such formation depends on the amount of Cl<sub>2</sub> in the ClO<sub>2</sub> and on the quantity of lignin remaining in the pulp (commonly expressed in “kappa numbers”). With high kappa numbers and more Cl<sub>2</sub> in the ClO<sub>2</sub>, the probability of forming PCDD/PCDF increases.

U.S. EPA scientists reported an average PCDD/PCDF concentration of 22.3 ng I-TEQ/kg in Kraft bleached pulp from five mills (Amendola *et al.* 1989). PCDD/PCDF concentrations ranging from 0.4 to 196 ng TEQ/kg, with a median of 8.8 ng TEQ/kg, were determined in pulp bleached using elemental chlorine or chlorine derivatives as reported in 1988 and a similar range, with a median of 7.6 ng WHO-TEQ/kg, as reported in 1996 (USEPA 2006a). The default emission factor is 10 µg TEQ/t of Kraft bleached pulp.

Chinese bleached pulps exhibited high concentrations of PCDD/PCDF (Zheng *et al.* 1997, 2000). Zheng *et al.* (2000) report 24.7 ng I-TEQ/kg of pulp for a C-E-H bleach sequence with a relatively “typical” chlorine bleach pattern (2,3,7,8-Cl<sub>4</sub>DF = 13.6 ng/kg and 2,3,7,8-Cl<sub>4</sub>DD = 2.0 ng/kg but high concentrations of 1,2,3,7,8-Cl<sub>5</sub>DD = 29.8 ng/kg and Cl<sub>6</sub>DD = 35.8 ng/kg). Zheng *et al.* (1997) also found high concentrations in five bleached pulp from non-wood fibers that ranged from 33.5 ng I-TEQ/kg to 43.9 ng I-TEQ/kg. These samples were characterized by very high concentrations of 2,3,7,8-Cl<sub>4</sub>DD, 1,2,3,7,8-Cl<sub>5</sub>DD, and 1,2,3,4,7,8-Cl<sub>6</sub>DD but had no quantifiable 2,3,7,8-substituted Cl<sub>4</sub>DF and Cl<sub>5</sub>DF.

Thermo-mechanical pulp (TMP) pulp in Sweden had concentrations of around 1 µg TEQ/t pulp and between 0.17 ng I-TEQ/kg and 1.65 ng I-TEQ/kg in Germany (Santl *et al.* 1994). The emission factor for TMP is 1 µg TEQ/t pulp.

Recycled papers from waste papers with low PCDD/PCDF content has an emission factor of 3 µg TEQ/t based on information provided by CORMA (2004) and recycled pulp/paper from impacted sources, *e.g.*, waste papers with high PCDD/PCDF content has an emission factor of 10 µg TEQ/t based on data by Santl *et al.* (1994).

Replacement of Cl<sub>2</sub> in the first bleaching stage by ClO<sub>2</sub> will dramatically reduce the formation of 2,3,7,8-Cl<sub>4</sub>DD and 2,3,7,8-Cl<sub>4</sub>DF and to 0.1-0.3 pg/g bleached pulp corresponding to 0.1-0.3 µg/t of bleached pulp.

Concentrations of PCDD/PCDF in Kraft bleached papers using free chlorine (Cl<sub>2</sub> gas) and the respective default emission factors are 5 µg TEQ/t for cosmetic tissues, shopping bags and other consumer papers and 2 µg TEQ/t for filter papers and newspapers from primary fibers. If chlorine dioxide or total chlorine-free bleaching is utilized, the emission factor will be 0.5 µg TEQ/t.

Sulfite papers using old technologies have an  $EF_{\text{Product}}$  of 1  $\mu\text{g TEQ/t}$  paper. Applying new technology will lower the emission factor to 0.1  $\mu\text{g TEQ/t}$ .

Unbleached papers have an emission factor of 0.5  $\mu\text{g TEQ/t}$ .

Recycling papers will have an emission factor of either 10  $\mu\text{g TEQ/t}$  for recycling papers originating from pulp made by the old Kraft process or 3  $\mu\text{g TEQ/t}$  for recycling papers made of primary papers made with modern bleaching technology.

### Release in Residues

A survey of pulp and paper mills in Canada found that total residues were generated at a rate greater than 80 kg/t of product and consisted of the following three types of residue (Elliott and Mahmood 2005):

- Wastewater treatment residues (sludges resulting from primary clarification, secondary treatment and deinking operations) with a generation rate of 50 kg/t;
- Fly ash and bottom ash from power and auxiliary boilers; and
- "Other inorganics" - electrostatic precipitator dust from boilers and recausticizing residues (lime mud), and grits and dregs.

Among mills of all types, newsprint mills with de-inking processes had the highest rate of residue generation, 148 kg/ADt, while newsprint mills with no de-inking had the lowest rate, 65 kg/ADt (Elliott and Mahmood 2005).

European companies report total waste generation rates from their pulp and paper mills that range from 23 to 163 kg/t of product, with a mean of 125 kg/t product (Monte *et al.* 2009). Of this total waste, the most significant waste streams include wastewater treatment sludges, lime mud, lime slaker grits<sup>21</sup>, green liquor dregs<sup>22</sup>, boiler and furnace ash, scrubber sludges and wood processing residuals. In general, wastewater treatment sludge constitutes the largest residual waste stream in terms of volume (Monte *et al.* 2009).

### Sludge

In 1989, a Canadian study reported concentrations of 2,3,7,8-TCDD ranging from 170 to 370 ng/kg in sludge from 10 pulp and paper mills (8 bleached Kraft mills and 2 sulfite mills (Clement *et al.* 1989).

At a recovered paper mill, Santl *et al.* (1994) found 24.9 and 44.37 ng TEQ/kg in two samples of the de-inking sludge and, in the wastewater treatment sludge, 11.01 ng I-TEQ/kg. In this Toolkit, an emission factor of 30  $\mu\text{g TEQ/t}$  sludge will be applied for the combined deinking and fiber sludges.

The concentrations in pulp sludge using old bleaching sequences is in the range from 2 ng TEQ/kg d.m. to 370 ng TEQ/kg d.m. with a median of 93 ng TEQ/kg sludge. The emission factor for bleached Kraft sludge is 4.5  $\mu\text{g TEQ/t}$  of bleached Kraft pulp. Alternatively, the concentration in the sludge of 100 ng I-TEQ/kg sludge can be used and multiplied with the total mass of sludge disposed of per year to calculate the annual release.

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<sup>21</sup> lime mud that pebbled in the kiln but did not calcine, from chemicals used in kraft pulp mills.

<sup>22</sup> matter which does not decant in green liquor clarifier.



Almost no difference in the concentrations of the sludge from wastewater treatment systems was found between mills using conventional delignification and those mills using oxygen delignification. The sludges have been analyzed for 2,3,7,8-substituted Cl<sub>4</sub>DD and Cl<sub>4</sub>DF as well as for all 17 2,3,7,8-substituted PCDD and PCDF congeners. The concentrations ranged from 3.8 ng TEQ/kg d.m. to 5.2 ng TEQ/kg d.m. for conventional delignification and from 1.8 ng TEQ/kg d.m. to 4.5 ng TEQ/kg d.m. for ED or ED/OD delignification.

With an estimated average of 4 ng TEQ/kg d.m., the default emission factor for pulp sludge using modern technology will be 0.2 µg TEQ/t of pulp.

Release vectors into the environment will be determined by the way the sludge is handled. Common disposal practices include landfill and surface impoundment, land application, recycling (compost, animal bedding) or incineration.

### Ash

Ash residuals generated from power boilers combusting wood residues, sludges, or auxiliary fuels constitute a major fraction of the solid residues produced by pulp and paper mills (Elliott and Mahood 2006). In some countries, such as Canada and the U.S., landfilling is the primary method of ash disposal (Elliott and Mahood 2006). Land application of ashes produced from salt-laden hog fuels at coastal pulp and paper mills is regulated for PCDD/PCDF.

U.S. EPA (2006a) derived an EF<sub>Residue</sub> for boiler ash of 13.2 µg I-TEQ/t of fuel, based on five NCASI studies in which wood, bark and sawdust were burned in boilers equipped with multicyclones or ESPs.

Based on data from Uloth and van Heek (2002) that describe the ash generation rates for power boilers burning clean hog fuel and the PCDD/PCDF concentrations of the ashes, an estimated average EF<sub>Residue</sub> of 15.6 µgTEQ/t of fuel can be calculated, as shown in Table III.47.3:

**Table III.47.3 Ash generation rates and PCDD/PCDF concentrations for power boilers at pulp and paper mills (Uloth and van Heek 2002)**

Power boilers burning clean hog fuel (with or without wastewater treatment plant sludge)	Grate or bottom ash	Multicyclone ash	for ESP, scrubber or combined flyash
PCDD/PCDF, µgTEQ/t ash	0.02	0.10	0.46
Ash generation rate, kg/t hog fuel	10-20	12-16	18-41
PCDD/PCDF release to residue, µgTEQ/t hog fuel (mean)	0.2-0.4 (0.35)	1.2-1.6 (1.4)	6.3-18.9 (13.8)
Mean total PCDD/PCDF release to residue, µgTEQ/t hog fuel	15.6		

In a Canadian study of boilers fired with salt-laden hog fuel, PCDD/PCDF concentrations in ashes were 3.80 µg TEQ/kg ash and, with the addition of 2-5% tire-derived fuel, 2.63 µg TEQ/kg (Duo *et al.* 2002). Using the first value and estimating a total ash generation rate of 60 kg/t, based on mean of the values

given in Table III.47.3, an  $EF_{\text{Residue}}$  of 228  $\mu\text{g TEQ/ADt}$  can be derived for ash when salt-laden hog fuel is burned.

The median and mean concentrations of PCDD/PCDFs in 43 fly ashes (ESP/wet scrubber or combined multiclone/ESP/scrubber ashes) from 24 boilers (16 U.S. and 8 Canadian) firing 100% inland wood residues in pulp mills and panel plants were of 0.46 and 5.35 ppt TEQ (where ppt TEQ corresponds to 10-12 g TEQ/g ash), respectively (range: 0.0 to 29.4) (Environment Canada 2002).

The disposal of ash should be described and PCDD/PCDF releases estimated to the greatest extent possible, *e.g.*, fractions sent to landfills, applied to land, etc.

## Annex 48 Complementary information to source categories 7b through 7e – Production and Use of Chemicals

### Overview of revisions of emission factors

New or revised emission factors are presented according to four source categories of production and use of chemicals: chlorinated inorganic chemicals, chlorinated aliphatic chemicals, chlorinated aromatic chemicals and other non-chlorinated inorganic chemicals.

### 7b Chlorinated Inorganic Chemicals

#### Elemental Chlorine Production

Three chlor-alkali processes are used industrially: mercury cell, membrane cell and diaphragm cell. BAT for new chlor-alkali plants is generally considered to be membrane cell or non-asbestos diaphragm cell (EU IPPCB 2011). General descriptions of the main production methods can also be found in the BAT&BEP Guidelines.

**EF<sub>Air</sub>:** An EF<sub>Air</sub> of ND is proposed for stand-alone chlor-alkali facilities.

**EF<sub>Water</sub>:** An EF<sub>Water</sub> of 0.002 µg TEQ/ECU has been derived for Class 2c chlor-alkali facilities, and 1.7 µg TEQ/ECU for Class 2b facilities based on Dyke and Amendola (2007). Of the seven plants that were not associated with the EDC/VCM/PVC chain, emission factors were calculated based on the published data and production rates estimated to be 98% of plant capacity for the relevant years. For four plants of the seven, EF<sub>Water</sub> was 0.0016 µg TEQ/ECU. USEPA (2004) cited a median PCDD/PCDF concentration of 120 pg TEQ/L wastewater from U.S. chlor-alkali facilities. An EF<sub>Water</sub> of 17 µg TEQ/ECU is recommended for Class 2a, approximately 10-fold higher than Class 2b.

**EF<sub>Product</sub>:** Data describing PCDD/PCDF concentrations in Cl<sub>2</sub> or its co-products, H<sub>2</sub> and NaOH, are not available, and an EF<sub>Product</sub> of ND is recommended.

**EF<sub>Residue</sub>:** For metal electrodes, Dyke and Amendola (2007) reported transfers to secure landfill that range from 0.2 to 18 µg TEQ/ECU capacity (Median = 1.1 µg I-TEQ/ECU capacity) based on data gathered in 2000 and 2002. In the intervening time, the four largest generators have been closed. The average of the remaining three was 0.22 µg I-TEQ/ECU capacity. Based on the assumption that production rates were 98% of capacity, the following were derived: for Class 2c, an EF<sub>Residue</sub> of 0.3 µg TEQ/ECU; Class 2b, 1.7 µg TEQ/ECU, based on the median, and Class 2a, 27 µg TEQ/ECU, based on the highest in the dataset are recommended.

For graphite electrodes<sup>23</sup>, PCDD/PCDF concentrations in sludge from chlor-alkali production using graphite electrodes have been reported as follows: up to 3,985 µg I-TEQ/kg in a sample from Germany (She and Hagenmeier 1994); from 13 to 28 µg N-TEQ/kg in three samples from Sweden (Rappe *et al.*

<sup>23</sup> Graphite electrodes were mostly eliminated in the late 1990s and are virtually extinct today. There are no graphite electrodes in use in the US, Europe or Japan. The Chinese Chlor-Alkali Industry Association and the Alkali Manufacturers Association of India confirm that there are no units operating with graphite electrodes in their countries. RusChlor notes that there are two facilities in the Russian Federation doing so, and they will be closed by 2014.

1991), and 21.65 µg I-TEQ/kg in one sample from China (Xu *et al.* 2000). For the Chinese dioxin release inventory, it is assumed that on average 50 kg of graphite sludge is generated per ton of alkali produced. With a default concentration of 20 µg TEQ/kg graphite sludge, an  $EF_{\text{Residue}}$  of 1,000 µg TEQ/t of chlor-alkali is proposed, based on the most recent data. However, Sweden estimates 2.5 kg graphite consumed per ton of NaOH produced. With the latter sludge generation rate, an  $EF_{\text{Residue}}$  of 40 µg TEQ/t can be derived.

## 7c Chlorinated Aliphatic Chemicals

### Ethylene Dichloride (EDC), Vinyl Chloride (VCM), and Polyvinyl Chloride (PVC)

The major processes in the production of ethylene dichloride (EDC), vinyl chloride (VCM), and polyvinyl chloride (PVC) are as follows:

**1. EDC production** is accomplished by two processes - direct chlorination and oxychlorination, which may be used in combination as the “balanced process”.

Direct chlorination of ethylene is the catalyzed reaction of ethylene with elemental chlorine to produce EDC and HCl. The reaction is carried out at relatively low-temperatures (50-70°C) and pressures that are 4-5 times normal atmospheric pressure. Ferric chloride ( $\text{FeCl}_3$ ) is commonly used as a catalyst, although chlorides of other metals (aluminum, copper, antimony) may also be used.

Oxychlorination of ethylene entails the reaction of ethylene with HCl and either air or oxygen in the presence of a catalyst (usually copper chloride) in a fixed-bed reactor or a fluidized-bed reactor to produce EDC and water.

The balanced process for EDC production consists, in effect, of linking the direct chlorination and oxychlorination processes by recovering HCl produced during EDC thermolysis or “cracking” and using it as a reactant in the production of EDC by oxychlorination. When no EDC or HCl is imported or exported, then the EDC unit is called a ‘balanced unit’. The balanced process is used at many modern EDC/VCM and EDC/VCM/PVC facilities; however, import of HCl and oversized oxychlorination units have become common in recent years.

**2. EDC purification** usually begins with a water quench followed by caustic scrubbing. The water is returned to the process or is steam stripped prior to transfer to a water treatment system. EDC is further purified by distillation and sent to temporary storage before being used to produce VCM.

**3. VCM production** is carried out by thermolytic dehydrochlorination (“cracking”) of EDC to produce VCM and HCl along with various by-products. Cracking furnaces typically operate at temperatures of 450- 650°C and pressures about 20 times normal atmospheric pressure.

**4. VCM purification** occurs via a distillation process that separates VCM from high boiling residues containing PCDD/PCDF and other by-products. These residues and by-products are typically incinerated or otherwise destroyed, and, in some cases, HCl produced during destruction is recovered and recycled.

**5. PVC production** entails polymerization of VCM to produce PVC resin by one of four routes - suspension, dispersion/emulsion, solution or bulk (mass) – with suspension as the predominant route. In suspension and dispersion polymerization, water is the reaction medium. Solution polymerization is

carried out in an organic solvent. In bulk polymerization, VCM itself is the reaction medium until the polymer precipitates and absorbs remaining monomer. The reaction finishes as polymerization in the solid polymer.

PCDD/PCDF formation in the oxychlorination process is well-acknowledged. However, PCDD/PCDF are also known to occur in thermal or combustion processes of the EDC/VCM/PVC production chain.

The following waste streams from the EDC, VCM and PVC production chain are among those that potentially contain PCDD/PCDF and/or release PCDD/PCDF to one or more vectors:

- Stack gases from vent and liquid/vent combustors, HCl furnaces, and, if allowed, flares (USEPA 2012);
- Treated wastewater, which is discharged to surface waters, and wastewater treatment residue (sludge), which is commonly sent to landfills or to on-site or off-site thermal oxidizers or combustors;
- Liquid residues from the oxychlorination process, which are generated at the rate of 25-40 kg/t VCM (EU IPPCB 2003), and are commonly sent to on-site or off-site thermal oxidizers or combustors;
- Spent fixed-bed oxychlorination catalyst, which is generated at rates of 10 to 200 g/t VCM in plants using this technology (EU IPPCB 2003). This material may be landfilled, although some manufacturers subject the catalyst to a thermal treatment to destroy organics associated with the solid support;
- Fluidized-bed oxychlorination catalyst, which undergoes attrition so that small particles are carried over to product vapor and washed out in quench water that is sent to wastewater treatment where the catalyst is captured in wastewater treatment residues;
- Coke, which is generated during EDC pyrolysis and removed at a rate of 0.1-0.2 kg/t VCM (EC 2003);
- Spent lime, which is used in some plants for VCM neutralization (EC 2003);
- Maintenance waste, which includes a lengthy list of materials such as process filter media, used activated carbon, packing/saddles from scrubbers, incinerator solids, solids from various process streams, etc. (Vinyl Institute 2002).

### Releases to air

These arise from:

- Combustion devices – vent and liquid/vent combustors and thermal oxidizers, halogen acid furnaces, flares, on-site hazardous waste incinerators and power boilers. Some of these devices are used to control process vent gases, gaseous emissions from processes residues such as heavy ends and, in the case of on-site incinerators, liquid and solid residues. Halogen acid furnaces and possibly other devices recover HCl as a salable or reusable product from these devices, while power boilers are used to generate heat and power.
- Certain process units, *e.g.*, gases from EDC pyrolysis furnaces are vented directly to air and gases from other processes may also be vented directly to air for limited periods of time in order to accommodate downtime and trips on pollution control systems (EC 2003).

No emission factors for releases to air due to direct venting from EDC pyrolysis furnaces and other processes are derived due to lack of information. Releases from on-site hazardous waste incinerators not considered part of the process are addressed in Source Group 1 – Waste Incineration, and flares and power boilers are addressed in Source Group 3 – Power Generation and Heating.

### PVC-only Vent Combustors

For U.S. facilities, PCDD/PCDF concentrations and emissions per ton of PVC capacity derived from measurements in stack gases of vent combustors at facilities that produce only PVC are shown in Table III.48.1 (Eastern Research Group 2011).

**Table III.48.1 PCDD/PCDF Concentrations in stack gases of PVC vent combustors and their release to air per ton of PVC at facilities in the U.S.**

PCDD/PCDF concentrations in stack gases (ng I-TEQ/m <sup>3</sup> )		PCDD/PCDF Emissions (µg/t PVC)	
Vinyl Institute (2002) at 7% O <sub>2</sub>	Eastern Research Group (2011) at 3% O <sub>2</sub>	Eastern Research Group Baseline (2011) <sup>A</sup>	Eastern Research Group after new emission limit <sup>B</sup> is in place (2011) <sup>C</sup>
Range; Average (Median)	Range; Average (Median)	Range; Average (Median)	Range; Average (Median)
0.0014-0.042; 0.013 (0.01)	0.0017-0.91; 0.08 (0.017)	0.000053-0.026; 0.005 (0.00061)	0.000053-0.020; 0.0023 (0.00050)

<sup>A</sup> Emission factors were derived for 13 PVC vent combustors, based on flue gas concentrations measured in 2010 under current practice and relevant production rates. Total air emission from these combustors was 3.58 x 10<sup>4</sup> µg TEQ/y. Production of PVC in 2010 was 14.0 billion pounds (6.36 million tons) and capacity was 7.26 million tons (CMAI 2011b) yielding a capacity utilization factor of 87.6%.

<sup>B</sup> 0.023 ng TEQ/Nm<sup>3</sup> at 3% O<sub>2</sub>.

<sup>C</sup> Combustors exceeding the limit were constrained to the new emission limit.

### Vent and Liquid/Vent Combustors or Thermal Oxidizers at EDC, EDC/VCM and EDC/VCM/PVC Production Facilities

Emissions to air from these processes come from combustion. Generally, combustor data is reported or regulated as a concentration in air; *e.g.*, ng TEQ/normal cubic meter (Nm<sup>3</sup>). Estimating the mass of PCDD/PCDF released to air thus requires knowledge of stack gas flow rates and hours of operation. Some EDC, EDC/VCM and EDC/VCM/PVC facilities operate liquid/vent combustors or thermal oxidizers and some operate vent-only combustors or thermal oxidizers. The latter operations may dispose of their liquid residues (heavy ends) in on-site hazardous waste incinerators or contract with others for such disposal.

**Table III.48.2 PCDD/PCDF concentrations in stack gases of EDC/VCM vent and liquid/vent thermal oxidizers and EDC/VCM vent combustors in the U.S. (Vinyl Institute 2002, Carroll Jr. *et al.* 2001)**

PCDD/PCDF Concentrations in Stack Gases of EDC/VCM Vent and Liquid/Vent Thermal Oxidizers and Combustors in the U.S.
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	(ng I-TEQ/m <sup>3</sup> )			
	Vinyl Institute (2002) at 7% O <sub>2</sub>		Carroll Jr. <i>et al.</i> (2001) at 7% O <sub>2</sub>	
	Range	Average (Median)	Range	Average (Median)
EDC/VCM Liquid and Liquid/Vent Thermal Oxidizers	0.034-6.4	1.38 (0.3)	0.034-1.5	0.43 (0.096)
EDC/VCM Vent Combustors	0.01-10.3	2.47 (0.59)	0.01-0.59	0.15 (0.031)

Based on these measurements generated in 1996, the Vinyl Institute calculated estimated emissions from liquid and liquid vent combustors as 3.7 g I-TEQ/yr and from vent combustors as 6.9 g I-TEQ/yr. No data was given as to the rate of production of EDC or VCM each of these system types was serving; thus a separate emission factor for each cannot be calculated. Normalizing the total TEQ emissions for total VCM production at the time (6,173,000 tons), yields 1.7 µg TEQ/t VCM (Carroll Jr. *et al.* 2001).

Det Norske Veritas validated that all the EDC/VCM plants that are signatories to the ECVI charter met the charter commitment of 0.1 ng TEQ/Nm<sup>3</sup> maximum in 2011 (Det Norske Veritas 2012). Plastics Europe has published ecoprofile information on a number of materials including VCM. Air emissions are listed as 4.16 x 10<sup>-8</sup> mg TEQ/kg VCM (0.042 µg TEQ/t VCM produced).<sup>24</sup>

#### Halogen Acid Furnaces (HAF)

For HAF at U.S. EDC, EDC/VCM and EDC/VCM/PVC production facilities, data obtained between 1995 and 2001 show median emissions of 0.06 ng TEQ/dscm (0.02-0.53 ng TEQ/dscm, average of three runs) for HAF (USEPA 2005). There are insufficient data to allow the derivation of emission factors for release to air. Consequently, releases are estimated based on stack gas flow rates and a concentration of 0.02 ng TEQ/dscm for Class 3 HAF, 0.06 ng TEQ/dscm for Class 2, and 0.53 ng TEQ/dscm for Class 1.

#### EF<sub>Air</sub> for Vent and Liquid/Vent Combustors or Thermal Oxidizers at EDC, EDC/VCM or EDC/VCM/PVC facilities

Either the suggested EF<sub>Air</sub> may be chosen, or an EF<sub>Air</sub> may be calculated by multiplying PCDD/PCDF concentration in the flue gas by flue gas flow rates, in m<sup>3</sup>/hour, and hours per year of operation.

- Class 1: an EF<sub>Air</sub> of 5 µg TEQ/t VCM based on Carroll *et al.* (2001) or a flue gas concentration of 5 ng TEQ/Nm<sup>3</sup> is used, a factor of 10 higher than Class 2.
- Class 2: an EF<sub>Air</sub> of 0.5 µg TEQ/t VCM or a flue gas concentration of 0.5 ng TEQ/Nm<sup>3</sup> is used, a factor of 10 higher than Class 3.
- Class 3: an EF<sub>Air</sub> of 0.05 µg/t VCM or a flue gas concentration of 0.1 ng TEQ/Nm<sup>3</sup> is used based on EU BREF (EU IPPC 2003).

#### EF<sub>Air</sub> for PVC-only facilities

<sup>24</sup> Ecoprofile data (2006) available at: <http://www.plasticseurope.org/plastics-sustainability/eco-profiles/browse-by-flowchart.aspx?LCAID=r42>

Similarly, either the given  $EF_{Air}$  can be used or air releases can be estimated by multiplying the value for PCDD/PCDF concentrations in the flue gas of these devices by their respective flue gas flow rates, and their respective hours per year of operation.

- Class 1: an  $EF_{Air}$  of 1  $\mu\text{g TEQ/ton PVC}$  or PCDD/PCDF concentration of 1  $\text{ng TEQ/Nm}^3$  is based on the highest baseline value reported by Eastern Research Group (and a factor of 10 higher than Class 2).
- Class 2: an  $EF_{Air}$  of 0.1  $\mu\text{g TEQ/ton PVC}$  or emission concentration limit of 0.1  $\text{ng TEQ/Nm}^3$ , a factor of 5 larger than Class 3.
- Class 3: PCDD/PCDF emission of 0.021  $\mu\text{g TEQ/ton PVC}$  constitutes the highest emission value in grams for a real plant still meeting the proposed US EPA emission concentration limit of 0.023  $\text{ng TEQ/Nm}^3$  (Eastern Research Group 2011, CMAI 2011b).

For VCM production, air emission factors for HCB and PCBs of 72  $\mu\text{g/t}$  and 8.9  $\mu\text{g/t}$ , respectively, have been derived in Japan for one facility (Iwata *et al.* 2008).

### Releases to water

Releases to water from the EDC/VCM/PVC production chain most commonly consist of treated effluents discharged from on-site, facility-wide wastewater treatment systems or systems that serve multiple facilities. Treatment of industrial wastewater commonly entails a sequence of processes: biological treatment, settling/clarification, equalization, neutralization, filtration, stripping (air and steam), chemical precipitation, and adsorption (USEPA 2004). The EU BREF (section 12.5.4.2) notes that BAT for water releases consists of extensive pre-treatment followed by final biological treatment that can achieve 0.1  $\text{ng TEQ/L}$  in effluent (EU IPPCB 2003). OSPARCOM and the ECVM charter (EU BREF section 12.4.7) cite 1  $\mu\text{g TEQ/ton}$  annual oxychlorination capacity as BAT and industry commitment respectively; total effluent water flow variation plant-to-plant is an important factor in relating these values.

The Vinyl Institute (Vinyl Institute 2002) reported PCDD/PCDF concentrations in treated wastewater from the U.S. EDC/VCM/PVC industry, as listed below, together with the respective emission factors.

- For EDC/VCM and EDC/VCM/PVC facilities: concentrations in wastewater of 3.0 to 6.6  $\text{pg I-TEQ/L}$ , with an average of 4.7  $\text{pg I-TEQ/L}$  (ND = DL/2; congeners detected in all samples), and emission factors of 0.0032 to 0.032  $\mu\text{g I-TEQ/t EDC}$ , with an average of 0.015  $\mu\text{g I-TEQ/t EDC}$ ; and
- For PVC only facilities, concentrations in wastewater of 0.0 to 2.0  $\text{pg I-TEQ/L}$ , with an average of 0.43  $\text{pg I-TEQ/L}$  (ND = 0; 4 of 6 samples with no detected congeners), and emission factors of 0.0 to 0.04  $\mu\text{g I-TEQ/t PVC}$ , with a average of 0.0083  $\mu\text{g I-TEQ/t PVC}$ .

Later, U.S. EPA requested more data from the industry, which was assessed as follows (USEPA 2004):

- For chlor-alkali, EDC, VCM, and other organic operations, concentrations in treated wastewater of 0.000104 to 110  $\text{pg I-TEQ/L}$ , with a median of 55.2  $\text{pg I-TEQ/L}$ ; and
- For EDC, VCM, and other organic operations, concentrations of 3.12 to 174  $\text{pg I-TEQ/L}$ , with a median of 34.3  $\text{pg I-TEQ/L}$ ; and



- PVC-only operations, one facility, 0.333 µg I-TEQ/L.

In 2007, The Vinyl Institute proposed to US EPA a voluntary program to measure PCDD/PCDF releases in wastewater discharges to surface waters from facilities manufacturing EDC by oxychlorination (Vinyl Chloride Producers 2007). In 2011, the results of the testing program were reported based on 2008/2009 data (Vinyl Chloride Producers 2011). The results demonstrated that each plant individually met the EU BREF limits. Summed across the 11 EDC/VCM plants tested<sup>25</sup>, the total release to water was 0.028 g I-TEQ/day, in comparison to the value of 0.049 g I-TEQ/day that can be calculated using the EU BREF (0.1 ng TEQ/L) BAT and the wastewater release rate. This emission (0.028 g I-TEQ/day) is noted as a maximum emission, utilizing the highest flow rate for process water, a highly variable stream.

At 0.028 g TEQ/day, the total release to water s from the 11 facilities is 10.2 g TEQ/yr. These same 11 facilities reported their total release to water as 5.96 g TEQ in the 2009 Toxics Release Inventory (USEPA 2012a).

In 2007, European EDC/VCM facilities reported releases to water ranging from 0.0037 to 1.65 µg TEQ/ton oxychlorination capacity (OSPAR 2009). In 2011, Det Norske Veritas reported that all the EDC/VCM facilities that are signatories to the ECVM charter met the charter commitment of 1 µg TEQ/ton oxychlorination, with data unavailable for one plant (Det Norske Veritas 2012).

#### **EF<sub>Water</sub> for EDC/VCM/PVC and EDC/VCM facilities:**

- Class 1: an EF<sub>Water</sub> of 25 µg TEQ/t EDC for sites with oxychlorination reactors or 5 ng TEQ/L effluent waste water can be used, a factor of 10 higher than Class 2.
- Class 2: an EF<sub>Water</sub> of 2.5 µg TEQ/t EDC for sites with oxychlorination reactors is presented, or 0.5 ng TEQ/L TEQ/L effluent waste water can be used, a factor of five higher than Class 3.
- Class 3: an EF<sub>Water</sub> of 0.5 µg TEQ/ton EDC by for sites with oxychlorination reactors or 0.1 ng TEQ/L effluent waste water is presented, based on OSPAR and the ECVM Charter.

#### **EF<sub>Water</sub> for Suspension and Dispersion/Emulsion PVC-only facilities:**

- Class 1: an EF<sub>Water</sub> of 0.03 µg TEQ/t PVC or concentration of 0.01 ng/L is presented, a factor of 10 higher than Class 2.
- Class 2: an EF<sub>Water</sub> of 0.003 µg TEQ/t PVC is presented, based on the average EF<sub>Water</sub> derived by the Vinyl Institute, utilizing 1995 emissions and standalone PVC capacity, with non-detects evaluated at zero, or concentration of 0.001 ng/L (Vinyl Institute 2002).
- Class 3: an EF<sub>Water</sub> of 0.0003 µg TEQ/t PVC or concentration of 0.0001 ng/L is presented, a factor of 10 lower than Class 2.

## **Releases to Land**

Releases to land can entail releases of residues to landfills, as well as releases to surface soils. Releases to surface soils from the EDC/VCM/PVC production chain are thought to be uncommon. However, the

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<sup>25</sup> There are 13 plants in the US practicing oxychlorination. At the time of testing, the Shintech plant was under construction. The Georgia Gulf plant in Lake Charles does not discharge to surface waters, and this is noted in the report.

Vinyl Institute (2002) reported that, in the U.S. as of 1996, 6% of wastewater treatment sludge was disposed of by application to surface soils – “land farming” (Vinyl Institute 2002). U.S. EPA (2006) attributed the release to land of 1.45 g I-TEQ to EDC/VCM/PVC manufacturing in 2000, due to land application of wastes from one facility that ended this practice that same year (USEPA 2006). Carroll Jr. *et al.* (2001) reported releases to land by one U.S. EDC/VCM/PVC facility using “land farm” for disposal of wastewater treatment sludge and derived emission factors from two samples of material at of 0.054 and 0.11  $\mu\text{g TEQ/t EDC}$  capacity. The average of these two emission factors is 0.08  $\mu\text{g TEQ/t EDC}$  capacity.

**EF<sub>Land</sub> for wastewater treatment sludge from EDC/VCM/PVC facilities:** An EF<sub>Land</sub> of 0.08  $\mu\text{g TEQ/t EDC}$  capacity (0.01  $\mu\text{g TEQ/t EDC}$  production) based on the findings by (Carroll Jr. *et al.* 2001) is presented to be used only for those individual facilities that use land application for disposal of wastewater treatment sludge.

## Releases to Product

### PVC Resin

In 1994, the Swedish EPA reported PCDD/PCDF concentrations of 0.86 and 4.70  $\mu\text{g TEQ/g}$  in two samples of suspension PVC from two Swedish PVC facilities (Swedish Environmental Protection Agency 1994). In 1996, Carroll *et al.* analyzed 26 resin samples and reported only two hepta-CDD and CDF congeners at concentrations above limits of quantification (detection limits were not reported and non-quantifiable concentrations were designated as “non-detects, ND”) in one sample of bottle resin. (Carroll *et al.* 1996, 1998) In 1998, Wagenaar *et al.* (1998) analyzed eleven PVC resin samples, and found only hepta- and octa- PCDD/PCDF at concentrations that were above limits of detection but below limits of quantification. LOQ was not reported. Thus NA is the emission factor for PCDD/PCDF in resins for class 3 and ND for classes 1 and 2.

#### **EF<sub>Product</sub> for PVC resin:**

- Class 1 and Class 2: ND
- Class 3: NA

### VCM

For VCM, the only journal-published work remains that of European producers (Isaksen *et al.* 1996) who analyzed six samples of VCM. Congeners were detected at the  $\text{ng/t}$  level; however, due to that extremely dilute concentration ( $\text{fg/g}$ ) the authors concluded that there are no process-generated PCDDs and PCDFs in VCM. There has been no more recent work to confirm or contradict this conclusion. Moreover, releases in VCM are relevant only for the very small fraction of VCM that is not used as monomer for PVC, so NA is presented as the EF<sub>Product</sub> for VCM.

#### **EF<sub>Product</sub> for VCM:**

- NA for all classes.

### EDC

The following emission factors are relevant only for EDC sold outside the EDC/VCM and EDC/VCM/PVC product chains:

**EF<sub>Product</sub> for EDC produced via oxychlorination or mixed oxychlorination/direct chlorination:**

- For Class 1: an EF<sub>Product</sub> of 2.0 µg TEQ/t EDC is presented, a factor of 10 greater than Class 2.
- For Class 2: an EF<sub>Product</sub> of 0.2 µg TEQ/t EDC is presented, based on the In-Process EDC sample reported by the Vinyl Institute.
- For Class 3: an EF<sub>Product</sub> of 0.006 µg TEQ/t EDC is presented, based on the average of the Sales EDC samples reported by (Carroll Jr. *et al.* 2001).

**EF<sub>Product</sub> for EDC derived from Direct Chlorination, and only for product sold outside the VCM product chain:**

- For all facilities, ND.

### Release to Residues

These are potentially the largest route of PCDD/PCDF release from EDC, VCM and PVC production, depending upon their treatment or destruction. Residues of greatest interest include process residues, wastewater treatment sludge, spent catalyst, and maintenance waste. Wastewater treatment sludge is reported to account for 26-33 percent of total PCDD/PCDF release from EDC/VCM/PVC production in the U.S.; spent catalyst, 19-25 percent; and maintenance waste, 12-20 percent (Vinyl Institute 2002).

Little is known about PCDD/PCDF levels in EDC/VCM/PVC process residues in part because they are commonly sent to liquid and liquid/vent thermal oxidizers or to on- or off-site incinerators. This may not always be the case. For example, heavy ends from Iranian EDC/VCM/PVC facilities have reportedly been sent to landfills (Ghaheri and Ghaheri 2007). Data compiled from European facilities show PCDD/PCDF concentrations ranging from 0.04 to 18 µg TEQ/kg in heavy ends from EDC/VCM production (Vinyl Institute 2002). In the U.S., concentrations of 6,365 µg TEQ/kg were measured in a sample of heavy ends from EDC distillation, 3.2 µg TEQ/kg in a waste sample described as heavy ends from VCM distillation, and 20 µg TEQ/kg in general process wastes (distillation residues, heavy ends, tars and reactor clean-out wastes) (Costner 1995, Stringer *et al.* 1995). Because of these high levels of contamination, the BAT&BEP Guidelines are clear: these streams must be destroyed to meet best practices.

**Wastewater treatment solids (WWTS):** A German EDC/VCM/PVC facility reported a PCDD/PCDF concentration of about 500 µg TEQ/t in WWTS (EU IPPCB 2003) which falls within the very broad range reported by the Vinyl Institute and presented in Table II.48.3, together with the respective emission factors.

The Vinyl Institute noted that PCDD/PCDF concentrations in WWTS from U.S. EDC/VCM facilities with fluidized bed oxychlorination reactors vary over a broader range and generally are higher than those from facilities with fixed bed oxychlorination reactors. In the Vinyl Institute study, ten WWTS samples were analyzed; two from PVC-only plants, four from fluidized bed oxychlorination plants and four from fixed bed oxychlorination plants (Carroll Jr. *et al.* 2001). The lowest concentration was found in the PVC-

only WWTS. The highest concentration of a fixed bed sample was 250 µg I-TEQ/t sludge. Three of the four fluidized bed samples exceeded that value, and ranged to 12,000 µg I-TEQ/t sludge.

Accordingly, the Vinyl Institute developed upper bound emission factors based on the highest release rate per ton of sludge: for the fixed bed catalyst facilities, 0.75 µg I-TEQ/t EDC (1.5 µg I-TEQ/t EDC via oxychlorination) and for fluidized bed facilities, 4.0 µg I-TEQ/t EDC (7.9 µg I-TEQ/t EDC via oxychlorination).<sup>26</sup> Most likely emission factors were also reported for fixed bed oxychlorination reactors (0.19 µg I-TEQ/t EDC) (0.37 µg I-TEQ/t EDC via oxychlorination) and fluidized bed reactors (1.96 µg I-TEQ/t EDC) (3.9 µg I-TEQ/t EDC via oxychlorination) (Table II.48.3). However, there was no clear difference between EDC/VCM and EDC/VCM/PVC facilities when the type of oxychlorination reactor - fixed bed or fluidized bed - was taken into account.

**Table III.48.3– PCDD/PCDF concentrations in and emission factors for wastewater treatment sludge from U.S. EDC/VCM, EDC/VCM/PVC and PVC-only facilities in the U.S. (Vinyl Institute 2002)**

Facility type	PCDD/PCDF content (µg I-TEQ/t sludge)		Emission Factor (µg I-TEQ/t EDC by oxychlorination or PVC)	
	Range	Average (Median)	Most likely	Upper bound
PVC only	2.8 - 5.5	3.9 (3.9) <sup>A</sup>	0.023 <sup>B</sup>	0.077 <sup>B</sup>
EDC/VCM, and EDC/VCM/PVC: Fixed bed oxychlorination reactors	93-12,000 <sup>C</sup>	2200 (310) <sup>C</sup>	0.37	1.5
EDC/VCM, and EDC/VCM/PVC Fluidized bed oxychlorination reactors			3.9	7.9

<sup>A</sup>Two samples only

<sup>B</sup>per ton PVC

<sup>C</sup>Both fixed bed and fluidized bed oxychlorination reactors.

**Spent catalyst:** EDC/VCM/PVC and EDC/VCM production generates spent catalysts as residues from EDC production by both direct chlorination and oxychlorination processes. Of these two the oxychlorination catalyst is most significant for PCDD/PCDF (EU IPPCB 2003).

**Oxychlorination:** The oxychlorination process is carried out in either fluidized-bed or fixed-bed reactors using a metal catalyst, typically copper chloride:

<sup>26</sup> The Vinyl Institute report estimated 1995 EDC production was 11,115,000 t. This is divided approximately equally between direct chlorination and oxychlorination. For oxychlorination, the report estimates that 5,400,000 t of EDC was produced at plants operating fixed bed technology and 5,600,000 t EDC produced at plants operating fluidized bed technology. The report characterized emission factors on the basis of total EDC production; however, in recent years, because the oxychlorination process is a much larger potential generator of PCDD/PCDF than the direct chlorination process, the convention has become to express emission factors associated with EDC in terms of oxychlorination production (OSPAR 2009). Thus, the values in the table are derived from the Vinyl Institute report, but metrics are converted from tons EDC production to tons oxychlorination production (emission factors multiplied by 2), on the assumption that half the EDC production is due to oxychlorination and PCDD/PCDF emission is attributed to that half.

- With fluidized-bed reactors, spent catalyst is removed continuously by the entrainment of fines that accumulate in sludge during wastewater treatment. The catalyst itself is seldom discarded.
- With fixed-bed reactors, spent catalyst is removed and collected as a discrete solid residue at the end of its useful life at a rate ranging from 10 to 200 g/t VCM (EU IPPCB 2003).

The Vinyl Institute (2002) reported PCDD/PCDF concentrations in oxychlorination catalyst ranging from 220 to 150,000  $\mu\text{g}$  I-TEQ/t, I-TEQ (median 15,000, average 29,000  $\mu\text{g}$  I-TEQ/t spent catalyst) and derived  $\text{EF}_{\text{Residue}}$  ranging from 0.018 to 8.1  $\mu\text{g}$  I-TEQ/t EDC (Vinyl Institute 2002).

Fixed bed catalyst sent to landfill was calculated to contain 4.7 g I-TEQ/yr and fluidized bed catalyst 0.21 g I-TEQ/yr. Dividing by EDC production from plants with fixed bed capacity (5,400,000 t/yr) gives 0.87  $\mu\text{g}$  I-TEQ/t EDC from fixed bed facilities and 0.045  $\mu\text{g}$  I-TEQ/t from plants with fluidized bed capacity (4,700,000 t/yr) (Vinyl Institute 2002).

**Coke and spent lime:** No PCDD/PCDF data were found for coke or spent lime.

**Maintenance wastes:** The Vinyl Institute (2002) surveyed all U.S. EDC/VCM manufacturing sites to identify the sources of process contaminated maintenance wastes and determined that the production of 11.115 million tons of EDC and 6.173 million tons of VCM was accompanied by the generation of 915.1 tons of maintenance wastes, of which, only 312 tons is sent to landfill (the rest is incinerated in normal course). This equates to a generation rate for maintenance waste of only 28 g waste/t EDC.

### **Waste Water Treatment Solids**

#### **$\text{EF}_{\text{Residue}}$ for EDC/VCM facilities for wastewater treatment solids:**

- For Class 1: an  $\text{EF}_{\text{Residue}}$  of 0.75  $\mu\text{g}$  TEQ/t EDC produced via fixed bed oxychlorination or 4  $\mu\text{g}$  TEQ/t EDC from sites with fluid bed oxychlorination is presented, representing the upper end of the distribution of plants in the Vinyl Institute study.
- For Class 2: an  $\text{EF}_{\text{Residue}}$  of 0.2  $\mu\text{g}$  TEQ/t EDC from sites with fixed bed oxychlorination or 2  $\mu\text{g}$  TEQ/t EDC from sites with fluid bed oxychlorination is presented, representing the most likely value in the distribution of plants in the Vinyl Institute study.
- For Class 3:  $\text{EF}_{\text{Residue}}$  of NA is accorded to facilities that incinerate wastewater treatment solids; for those that do not, 0.095  $\mu\text{g}$  TEQ/t EDC from sites with fixed bed oxychlorination and 0.4  $\mu\text{g}$  TEQ/t EDC from sites with fluid bed oxychlorination based on the lower values and the ratio between the two types in the Vinyl Institute (2002).

#### **$\text{EF}_{\text{Residue}}$ for PVC-only facilities, wastewater treatment solids:**

- For Class 1: an  $\text{EF}_{\text{Residue}}$  of 0.095  $\mu\text{g}$  TEQ/t PVC is based on the highest value derived by the Vinyl Institute (2002).
- For Class 2: an  $\text{EF}_{\text{Residue}}$  of 0.06  $\mu\text{g}$  TEQ/t PVC is based on the average of the values derived by the Vinyl Institute (2002).
- For Class 3: an  $\text{EF}_{\text{Residue}}$  of NA is presented for facilities that incinerate waste water treatment solids or 0.005  $\mu\text{g}$  TEQ/t PVC for those that do not is presented, based on the lowest value derived by the Vinyl Institute (2002).

**EF<sub>Residue</sub> for EDC/VCM facilities with fixed-bed oxychlorination, as spent catalyst:**

- Class 1: an EF<sub>Residue</sub> of 8 µg I-TEQ/t EDC based on the highest value derived by the Vinyl Institute.
- Class 2: an EF<sub>Residue</sub> of 0.85 µg I-TEQ/t EDC is the average of the values derived by the Vinyl Institute.
- Class 3: an EF<sub>Residue</sub> of NA is presented for facilities that thermally treat or incinerate spent catalyst; for those that do not, 0.02 µg I-TEQ/t EDC is presented, which is the lowest of the values derived by the Vinyl Institute.

**Maintenance Waste**

**EF<sub>Residue</sub> for maintenance waste sent to landfill from EDC/VCM facilities:**

- In lieu of an EF<sub>Residue</sub>, a surrogate of 15,000 µg/t waste, the median of the values reported for spent catalyst, as reported by the Vinyl Institute can be used in conjunction with actual waste generation rates or a surrogate of 28 g waste/t EDC capacity to estimate PCDD/PCDF release in maintenance waste.

**Table III.48.4 Emission factors for EDC/VCM and EDC/VCM/PVC production**

Class	µg TEQ/t VCM	µg TEQ/t EDC from Sites with Oxychlorination Reactors <sup>A</sup>				µg TEQ/t Product		
			WWTS <sup>B</sup>					
	Liquid and Liquid/Vent Combustors	Treated Waste water	Fixed Bed	Fluid-ized Bed	Spent Catalyst, Fixed Bed Oxychlorination	EDC <sup>C</sup>	VCM	PVC
1	5	25	0.75	4.0	8	2	NA	ND
2	0.5	2.5	0.2	2.0	0.85	0.2	NA	ND
3	0.05	0.5	0.095	0.4	0.02 <sup>D</sup>	0.006	NA	NA

<sup>A</sup>Assumes a balanced or nearly balanced direct chlorination-oxychlorination process. Sites operating direct chlorination only are ND.

<sup>B</sup>Wastewater Treatment Solids.

<sup>C</sup>Derived from oxychlorination or mixed direct chlorination and oxychlorination and sold for applications other than vinyl chloride. EDC derived from direct chlorination alone is NA.

<sup>D</sup>Zero if combusted to remove organics.

**Table III.48.5 Emission factors for PVC-only facilities**

Class	µg TEQ/t PVC Product			
	Air	Water	Wastewater Treatment Solids	Product
1	1	0.03	0.095	ND
2	0.1	0.003	0.06	ND
3	0.02	0.0003	0.005	NA

## 7d Chlorinated Aromatic Chemicals

### Chlorobenzenes

In evaluating production of chlorobenzenes by direct chlorination of benzene, Liu *et al.* (2004) determined PCDD/PCDF concentrations in collected six samples from the production process, as shown in Table III.48.6:

**Table III.48.6 Concentrations of PCDD/PCDF in chlorobenzenes, intermediate and residue (Liu *et al.* 2004)**

Sample	PCDD/PCDF (ng TEQ/kg)
Intermediate: mixture of 1,2- and 1,4-dichlorobenzene after distillation and separation from monochlorobenzene	620
Intermediate: mixture of di- and trichlorobenzenes	1850
Residue left from purification of 1,2,4-trichlorobenzene	3370
1,4-Dichlorobenzene: after distillation and crystallization (98.1%)	39
1,2-Dichlorobenzene: after distillation and crystallization	ND
Purified 1,2,4-trichlorobenzene	ND

Although no PCDD/PCDF were detected in 1,4-dichlorobenzene, total PCBs were present at a concentration of 1,797 ng/g. No information is available on releases to air or water.

Based on this study by Liu *et al.* (2004), the following emission factors are presented:

**EF<sub>Product</sub>**: 39 µg TEQ/t for 1,4-dichlorobenzene.

### Pentachlorophenol (PCP) and, Sodium Pentachlorophenate (PCP-Na)

Based on the analysis of PCP-Na, the Republic of China (2007) reported a PCDD/PCDF release of 25 g I-TEQ in 2,000 t of PCP-Na product, which indicates an EF<sub>Product</sub> of 12,500 µg I-TEQ/t. In 2010, Tondeur *et al.* (2010) determined an average PCDD/PCDF content of 634 mg TEQ/kg in 20 samples of PCP from a U.S. production facility. In 1994, Bao *et al.* (1994) detected PCDD/PCDF levels ranging from 612-924 mg I-TEQ/g in thermolysis waste from PCP and PCP-Na production at a Chinese facility.

Data are inadequate to support the derivation of EF<sub>Air</sub> and EF<sub>Water</sub>.

**EF<sub>Product</sub>**: For PCP, an EF<sub>Product</sub> of 634,000 µg TEQ/t is presented, based on Tondeur *et al.* (2010).

**EF<sub>Product</sub>**: For PCP-Na, an EF<sub>Product</sub> of 12,500 µg TEQ/t is presented, based on data from the Republic of China (2007).

Further, Bao *et al.* (1994) calculate an EF<sub>Residue</sub> of 768,000,000 µg TEQ/t for PCP and PCP-Na production via alkaline hydrolysis of HCH, a process which is no longer in use.

### 2,4,5-Trichlorophenoxyacetic Acid (2,4,5-T) and 2,4,6-Trichlorophenol

The highest concentration of 2,3,7,8-TCDD reported in a 2,4,5-T product from Germany was 7,000 ng I-TEQ/kg. In one sample of 2,4,6-trichlorophenol, PCDD/PCDF were found at 680,000 ng I-TEQ/kg (NATO/CCMS 1992).

Due to lack of data, emission factors have been derived only for releases in products:

**EF<sub>Product</sub>**: For 2,4,5-trichlorophenoxyacetic acid, an EF<sub>Product</sub> of 7,000 µg TEQ/t is presented (EC 1999b, NATO/CCMS 1992).

**EF<sub>Product</sub>**: For 2,4,6-trichlorophenol, an EF<sub>Product</sub> of 700 µg TEQ/t is presented (NATO/CCMS 1992, Fiedler 2003).

### Chloronitrofen, Chlornitrofen or 2,4,6-Trichlorophenyl-4-nitrophenylether (CNP)

Masunaga (1999) reported a PCDD/PCDF concentration in samples of chloronitrofen of 7,100 ng I-TEQ/g active ingredient in a batch produced in 1978; 11,300 ng I-TEQ/g in a 1983 batch; 62 ng I-TEQ/g in a 1986 batch; 4.1 ng I-TEQ/g in a 1987 batch; and 4.9 ng I-TEQ/g in a 1989 batch. There is no further information on the synthesis and what might have led to decreased contamination in the more recent batches. Due to lack of information, only emission factors for release in products are presented.

**EF<sub>Product</sub>**: For CNP produced using old technologies, an EF<sub>Product</sub> of 9,200,000 µg TEQ/ton is presented, based on the concentrations reported for the two oldest samples analyzed by Masunaga (1999).

**EF<sub>Product</sub>**: For CNP produced using new technologies, an EF<sub>Product</sub> of 4,500 µg TEQ/ton is presented, based on the concentrations reported for the two most recently produced samples that were analyzed by Masunaga (1999).

### Pentachloronitrobenzene (PCNB) (Quintozene)

PCB emission factors for PCNB production are shown in table III.48.7 below.

**Table III.48.7 DL-PCB emission factors for source category 7d Pentachloronitrobenzene (PCNB, Quintozene)**

7d	Pentachloronitrobenzene (PCNB, Quintozene)	Emission Factors (µg TEQ/t PCNB)				
		Air	Water	Land	Product	Residue
	<b>Classification</b>					
1	Low-end technologies	ND	ND	ND	2,400	ND
2	Mid-range technologies	ND	ND	ND	1,500	ND
3	High-end technologies	ND	ND	ND	680	ND

PCDD/PCDF concentrations ranging from 2.5 to 5.6 ng TEQ/g of PCNB, with a mean of 3.9 ng TEQ/g, were measured in three PCNB formulations in Australia (Holt *et al.* 2010). Use of PCNB for agricultural purposes in Australia was reported to be accompanied by the release to land of an estimated 27 g TEQ/year and ranking it as Australia's sixth largest source (Holt *et al.* 2010). Concentrations of PCDD/PCDF and dioxin-like PCBs that were determined in five Chinese PCNB product samples are shown



in Table III.48.8 (Huang *et al.* 2012). Hexachlorobenzene has also been identified as a contaminant in PCNB (USEPA 2010a).

**Table III.48.8 Concentrations of PCDD/PCDF and DL-PCBs in two “raw pesticide” samples (R-1 and R-2) and samples of three PCNB formulations (F-1, F-2, and F-3)**

		PCDD/PCDF, ng TEQ/g*	PCB, ng TEQ/g*
R-1	95% PCNB	0.26	0.68
R-2	95% PCNB	0.96	2.4
F-1	40% PCNB	0.18	2.0
F-2	30% PCNB, 15% Bromothalonil	0.73	0.82
F-3	20% PCNB, 20% Thiram	0.38	1.6

\*Each value is the mean of lower bound values obtained from the analysis of duplicate samples.

In addition, the Ministry of Agriculture, Forestry and Fisheries (MAFF) of Japan reported PCDD/PCDF at 3.7 ng TEQ/g of PCNB and dioxin-like PCBs at 0.86 ng TEQ/g PCNB in Japanese PCNB formulations (MAFF 2002).

The following emission factors are derived:

**EF<sub>Product</sub> for PCDD/PCDF:** 260 µg TEQ/t for PCNB produced by Class 3 facilities, based on the lowest value reported in the three studies, which was obtained by Huang *et al.* (2012); 2,600 µg TEQ/t for Class 2 facilities, based on the mean of the values reported in the three studies; and 5,600 µg TEQ/t for Class 1, based on the high value obtained by Holt *et al.* (2010). For agricultural uses of PCNB, each of these emission factors can also be used as **EF<sub>Land</sub>**.

**EF<sub>Product</sub> for DL-PCBs:** 680 µg TEQ/t for PCNB produced by Class 3 facilities, based on the lowest value reported by Huang *et al.* (2012); 1,500 µg TEQ/t for Class 2 facilities, based on the mean of the high and low values reported by Huang *et al.* (2012); and 2,400 µg TEQ/t for Class 1, based on the high value reported by Huang *et al.* (2012). For agricultural uses of PCNB, each of these emission factors can also be used as **EF<sub>Land</sub>**.

### 2,4-Dichlorophenoxyacetic Acid and its Derivatives

PCDD/PCDF were detected in 2,4-D as long ago as 40 years (Woolson *et al.* 1972) and as recently as 2012 (A. Grochowalski, personal communication, 4 October 2012, Gullett *et al.* 2012). In the U.S., agricultural use of 2,4-D was associated with the release to land of 28.9 g TEQ/year in 1995. Lack of information prevented the preparation of a more recent estimate (USEPA 2006a).

As shown in Table III.48.9, PCDD/PCDF concentrations in 2,4-D and its derivatives have ranged from non-detect to 6,800 ng/kg of 2,3,7,8-TCDD, the most potent of the PCDD/PCDFs. As might be expected, PCDD/PCDF concentrations have generally diminished over the 40 years for which data are available. However, recent studies show that significant concentrations of PCDD/PCDF continue to be found in 2,4-D and its derivatives. For example, during 2008-2012, PCDD/PCDF were measured in samples of 2,4-D, 2,4-D esters and 2,4-dichlorophenol feedstock from a production facility in Eastern Europe. For 31 samples of 2,4-D produced primarily for export, a mean concentration of 102.7 pg TEQ/g was determined, while 21 samples of 2,4-D that had an unknown fate had a mean concentration of 5,688 pg

TEQ/g. For both sample sets, most of the 2,4-D was produced on-site. However, beginning in 2010, crude 2,4-D was also imported from Asia for reprocessing. In addition, 51 samples of a variety of 2,4-D esters had a mean PCDD/PCDF concentration of 661.1 pg TEQ/g, and 17 samples of 2,4-dichlorophenol used as primary feedstock for production of 2,4-D and 2,4-D esters at this facility had a mean concentration of 116,365 pg TEQ/g (A. Grochowalski, personal communication, 4 October 2012).

**Table III.48.9 PCDD/PCDF concentrations in 2,4-Dichlorophenoxyacetic acid (2,4-D) and its derivatives**

	ng TEQ/kg	Point of production/purchase	Reference
2,4-D	<1,000 of 2,3,7,8-TCDD	Canada	Cochrane <i>et al.</i> (1981)
	6,800 of 2,3,7,8-TCDD	Germany	Hagenmaier (1986)
	4,800	Germany	Wilken <i>et al.</i> (1992)
	0–16	Japan	Masunaga <i>et al.</i> (2001)
	0.12-1.8	Australia	Holt <i>et al.</i> (2010)
	160-180		
	~300* (est.)***	U.S.	Gullett <i>et al.</i> (2012)
	5.43 – 405	Eastern Europe	Grochowalski (2012)
1,080-18,500			
Mixture of 2,4-D esters	661.1	Eastern Europe	Grochowalski (2012)
2,4-D dimethylamine salt	4,110	Germany	Wilken <i>et al.</i> (1992)
	160	Russia	Schechter <i>et al.</i> (1993)
2,4-D dimethylamine, 46.9%	8.7*	U.S.	Huwe <i>et al.</i> (2003)
2,4-D isooctyl ester, 61.7%	731*	U.S.	Huwe <i>et al.</i> (2003)
2,4-D isooctyl ester, 66.2%	2,627*	U.S.	Huwe <i>et al.</i> (2003)
2,4-D isooctyl ester, 67.2%	27.7*	U.S.	Huwe <i>et al.</i> (2003)
2,4-D isooctyl ester, 88.8%	1,379*	U.S.	Huwe <i>et al.</i> (2003)
Technical 2,4-D and 2,4-D Ester Herbicides	700**	U.S.	USEPA (2005)
2,4-D Herbicides purchased in U.S.	1.9*, 2.4*, 82.3*	U.S.	Schechter (1998)
2,4-D Herbicides purchased in Palestine and Israel	96.4* 828*	Palestine and Israel	Schechter (1998)
2,4-D Herbicide, Chimprom, Ufa, Russia	142*	Russia	Schechter (1998)

\* ng TEQ/kg of ready-for-use product (active ingredient plus adjuvants).

\*\* OCDD and OCDF were not assayed in 8 samples submitted by U.S. producers.

\*\*\* In as-purchased 2,4-D, Gullett *et al.* (2012) determined a  $\Sigma$ TCDF concentration of about 10 ng/g and noted that this value is consistent with Holt *et al.* (2010) and Masunaga *et al.* (2001). In two samples of

as-purchased 2,4-D, Holt *et al.* (2010) reported mean concentrations of  $\Sigma$ TCDF of 0.135 and 2.6 ng/g that were associated with PCDD/PCDF lower-bound values of 0.0004355 and 0.0775 ng TEQ/g, respectively. Based on the ratios of  $\Sigma$ TCDF to total TEQ for the samples from Holt *et al.* (2010), total PCDD/PCDF of 0.30 ng TEQ/g can be estimated for this sample of as-purchased 2,4-D.

**EF<sub>Product</sub> for PCDD/PCDF:** 0.12  $\mu$ g TEQ/t for 2,4-D and its derivatives that are produced by Class 3 facilities, based on the lowest value reported by Holt *et al.* (2010); 170  $\mu$ g TEQ/t for 2,4-D and its derivatives that are produced by Class 2 facilities, based on the mean of the higher-range values reported by Holt *et al.* (2010); 5,688  $\mu$ g TEQ/t for 2,4-D and its derivatives that are produced by Class 1 facilities, based on the mean value reported by Grochowalski (2012).

### Chlorinated Paraffins (CPs)

PCB and HCB emission factors for the production of CP are shown in tables III.48.10 and III 48.11 below:

**Table III.48.10 PCB emission factors for source category 7d Chlorinated Paraffins**

7d	Chlorinated Paraffins	Emission Factors (mg/t product)				
		Air	Water	Land	Product	Residue
1	Low-end production technologies	ND	ND	ND	210,000	ND
2	Mid-range production technologies	ND	ND	ND	165,000	ND
3	High-end production technologies	ND	ND	ND	40	ND

**Table III.48.11 HCB emission factors for source category 7d Chlorinated Paraffins**

7d	Chlorinated Paraffins	Emission Factors (mg/t product)				
		Air	Water	Land	Product	Residue
1	Low-end production technologies	ND	ND	ND	8,900	ND
2	Mid-range production technologies	ND	ND	ND	7,500	ND
3	High-end production technologies	ND	ND	ND	7	ND

Three samples of technical grade CPs from an East Asian country (with legislation in place limiting PCDD/PCDF in chemicals and products) were analyzed in duplicate, yielding lower-bound PCDD/PCDF concentrations that ranged from 132.9 to 545.4 pg TEQ/g and, mean concentrations for the three samples of 140.6, 228.6 and 490.8 pg TEQ/g (Takasuga *et al.* 2012).

In the same study, six samples of CPs produced from another East Asian country were found to have total PCB concentrations ranging from 140,000 to 210,000 ng/g, with a mean of 165,000 ng/g, as well as HCB concentrations ranging from 6,100 to 8,900 ng/g, with a mean of 7,733 ng/g. Considerable lower levels of PCB (40 ng/g) and HCB (7 ng/g) were detected in one sample from the East Asian country with legislation in place limiting PCDD/PCDF in chemicals and products.

In analyzing polyurethane foam and rubber materials used in a high volume air sampler pump, Takasuga *et al.* (2012) also detected high levels of PCBs and HCB in both of these materials and determined the main source of these contaminants as long-chain CPs that were produced in China and used in the

rubber at levels of 2-6% as a flame retardant. Subsequent analysis of the technical CP used in the rubber found concentrations of total PCBs of 140-190 ppm and 6.8-8.7 ppm HCB. Polychlorinated naphthalenes (PCNs) and pentachlorobenzene (PCBz) were also detected in the rubber but were not quantified.

The following emission factors are derived:

**EF<sub>Product</sub> for PCDD/PCDF:** 140 µg TEQ/t for CPs produced by Class 3 facilities, based on the lowest value reported by Takasuga *et al.* (2012); and 500 µg TEQ/t for Class 2, based on the mean of the values obtained with the most contaminated of the three samples.

**EF<sub>Product</sub> for PCBs:** 40 mg/t for CPs produced by Class 3 facilities, based on the lowest value reported by Takasuga *et al.* (2012a); 156,000 mg/t for Class 2 facilities, based on the mean of the values for five samples analyzed by Takasuga *et al.* (2012); and 210,000 mg/t for Class 1, based on the most contaminated of the samples analysed.

**EF<sub>Product</sub> for HCB:** 7 mg/t for CPs produced by Class 3 facilities, based on the lowest value reported by Takasuga *et al.* (2012a); 7,500 mg/t for Class 2 facilities, based on the mean of the values for the five samples analyzed by Takasuga *et al.* (2012); and 8,900 mg/t for Class 1, based on the most contaminated of the samples analyzed.

### ***p*-Chloranil (2,3,5,6-tetrachloro-2,5-cyclohexadiene-1,2-dione)**

Ni *et al.* (2005) analyzed chloranil produced by two Chinese facilities and found PCDD/PCDF concentrations of 13 and 126 ng I-TEQ/kg. The disparity in their results was attributed to the use of different production methods, which were not described.

Liu *et al.* (2012) determined PCDD/PCDF concentrations in chloranil samples from three other Chinese facilities, each of which used a production process involving the chlorination of hydroquinone. However, at each facility, the chloranil was purified to a different extent because of different intended uses. Chloranil produced for use as an intermediate in pharmaceutical products was most stringently purified and had a PCDD/PCDF concentration of 163 pg I-TEQ/g. PCDD/PCDF was found at 1,540,200 pg I-TEQ/g in the chloranil intended for use as an intermediate for dyes and pesticides. A PCDD/PCDF concentration of 26,368 pg I-TEQ/g was measured in moderate quality chloranil. Liu *et al.* (2012) proposed the average of these three values, 522,000 µg I-TEQ/t, as EF<sub>Product</sub> for chloranil. Total PCB levels in the three chloranil samples ranged from 1,179.4 to 12,413.7 pg/g (1.9-3.3 pg WHO-TEQ/g); pentachlorobenzene (PeCBz) ranged from 12.1 to 31.8 ng/g; and HCB from 3.8 to 391.5 ng/g.

No information is available to support the derivation of emission factors for releases to air, water, land and residue for chloranil. However, it is apparent that releases to residues will be greater with increasingly stringent purification.

Based on the findings of Ni *et al.* (2005) and Liu *et al.* (2012), the following emission factors are presented for *p*-chloranil production via chlorination of hydroquinone:

**EF<sub>Product</sub>:** For minimal purification of chloranil, an EF<sub>Product</sub> of 1,500,000 µg TEQ/t is presented.

**EF<sub>Product</sub>:** For moderate purification of chloranil, an EF<sub>Product</sub> of 26,000 µg TEQ/t is presented.

**EF<sub>Product</sub>:** For high purification of chloranil, an EF<sub>Product</sub> of 150 µg TEQ/t is presented.

An  $EF_{\text{Product}}$  of 400,000  $\mu\text{g TEG/t}$  product is presented for *p*-chloranil production via direct chlorination of phenol (Fiedler 1998, 1996, BUA 1992).

### Phthalocyanine pigments and dyes

HCB emission factors for the production of phthalocyanine pigments and dyes are included in Table III.48.12 below:

**Table III.48.12 HCB emission factors for source category 7d – Phthalocyanine Pigments and Dyes Production**

7d	Phthalocyanine-derived pigments and dyes	Emission Factors (g/t product)				
		Air	Water	Land	Product	Residue
	<b>Classification</b>					
1	Pigment Green 7 (CAS 1328-53-6)	ND	ND	ND	200	ND
2	Pigment Green 7 (BAT)	ND	ND	ND	10	ND
3	Pigment Green 36 (CAS 14302-13-7)	ND	ND	ND	10	ND
4	Pigment Green 36 (BAT)	ND	ND	ND	1	ND

As for PCDD/PCDF, these were detected in phthalocyanine copper and phthalocyanine green at concentrations of 73.28 and 1379.55 ng I-TEQ/kg, respectively, by Ni *et al.* (2005) No information was available to support the derivation of emission factors for releases to air, water, land and residue. Based on the values reported by Ni *et al.* (2005), the following emission factors for PCDD/PCDF release to products for the two phthalocyanine-based pigments and dyes are presented:

$EF_{\text{Product}}$  for phthalocyanine copper: 0.07  $\mu\text{g TEQ/kg}$ ; and

$EF_{\text{Product}}$  for phthalocyanine green: 1.4  $\mu\text{g TEQ/kg}$ .

### Tetrachlorophthalic acid (TCPA) and related pigments

TCPA is the primary feedstock for the production of a range of pigments. While no PCDD/PCDF data are available for TCPA, unintentional HCB concentrations as high as 3,000 ppm have been detected (Government of Japan 2006). However, BAT levels of less than 200 ppm and below 50 can be achieved by modification of production processes and recrystallization (Government of Japan 2006; Table III.48.13). With TCPA use, unintentional HCB is transferred to pigments and residues (Government of Japan 2007, 2006). TCPA-derived pigments include *e.g.* Pigment Yellow 110 (CAS 5590-18-1), Pigment Yellow 138 (CAS 30125-47-4), Solvent Red 135 and Solvent Red 162 (CAS 20749-68-2 and 71902-17-5).

**Table III.48.13 HCB emission factors for source category 7d TCPA and related pigments**

7d	TCPA and related pigments	Emission Factors (g/t product)				
		Air	Water	Land	Product	Residue
	<b>Classification</b>					
1	Tetrachlorophthalic acid (CAS 632-58-6)	ND	ND	ND	2000	ND
2	Tetrachlorophthalic acid (BAT)	ND	ND	ND	200	500
3	Solvent Red 135 (CAS 20749-68-2)	ND	ND	ND	200	ND
4	Solvent Red 135 (BAT)	ND	ND	ND	10	ND
5	Pigments Yellow 110 (CAS 5590-18-1) & 138	ND	ND	ND	200	ND

	(CAS 30125-47-4)					
6	Pigment Green 7 (CAS 1328-53-6)	ND	ND	ND	200	ND
7	Pigment Green 7 (BAT)	ND	ND	ND	10	ND
8	Pigment Green 36 (CAS 14302-13-7)	ND	ND	ND	10	ND
9	Pigment Green 36 (BAT)	ND	ND	ND	1	ND

These emission factors are associated with a medium level of confidence, as they are based on a low data range; they are not based on expert judgment, but are derived from a limited geographical coverage.

### Dioxazine dyes

Three dioxazine-based dyes that were produced using PCDD/PCDF-contaminated chloranil were analyzed by Williams *et al.* (1992) and found PCDD/PCDF concentrations as follows:

- Blue 106 (three samples): 19.5, 30.2 and 56.4 µg TEQ/kg;
- Blue 108: 0.1 µg TEQ/kg; and
- Violet 23 (Carbazole violet) (six samples): 1.4, 2.7, 2.7, 12.7, 16.0, and 18.9 µg TEQ/kg.

No data were available to support the derivation of emission factors for releases to air, water, land, and residue from the production of these dioxazine-based dyes.

Based on the values determined by Williams *et al.* (1992), emission factors for releases to product for these three dioxazine-based dyes are presented:

**EF<sub>Product</sub>** for Blue 106: 35 µg TEQ/kg;

**EF<sub>Product</sub>** for Blue 108: 0.1 µg TEQ/kg; and

**EF<sub>Product</sub>** for Violet 23 (Carbazole violet): 12 µg TEQ/kg.

### Triclosan [(5-chloro-2-(2,4-dichlorophenoxy)phenol)]

PCDD/PCDF have been detected in triclosan, sometimes at relatively high concentrations. Menoutis and Parisi (2002) determined concentrations of 2,3,7,8-TCDD and 2,3,7,8-TCDF in triclosan samples from six producers in India and China and obtained results shown in Table III.48.14.

**Table III.48.14 Concentrations of 2,3,7,8-TCDD and 2,3,7,8-TCDF in Triclosan produced in India and China**

Sample	Origin	2,3,7,8-TCDD (pg/g)	2,3,7,8-TCDF (pg/g)	pg I-TEQ/g
1	India	17.2	0.70	17.27
2	China	95.4	7.13	96.1
3	India	111.8	3.43	111.2
4	India	41.5	8.51	42.4
5	India	1712.0	0.43	1712
6	India	18.9	207.3	39.6

More recently, Ni *et al.* (2005) measured a PCDD/PCDF concentration of 5.03 ng TEQ/kg from a Chinese producer, attributing this relatively low value to the use of raw materials that were not favorable to PCDD/PCDF formation. Zheng *et al.* (2008) included this value along with those obtained by other researchers in reporting PCDD/PCDF concentrations of 0.8 to 5.03 ng TEQ/kg in Triclosan produced in China.

No information was available to allow derivation of emission factors for releases to air, water, land and residue.

**EF<sub>Product</sub>** using low-end production technologies: 1700 µg TEQ/t, based on the highest value from Menoutis and Parisi (2002).

**EF<sub>Product</sub>** using mid-level production technologies: 60 µg TEQ/t of product, based on the five lowest values from Menoutis and Parisi (2002).

**EF<sub>Product</sub>** using advanced production technologies: 3 µg TEQ/t of product, based on the values reported in Zheng *et al.* (2008).

## 7e Other Chlorinated and Non-Chlorinated Chemicals

### Titanium tetrachloride (TiCl<sub>4</sub>) and Titanium Dioxide (TiO<sub>2</sub>)

Titanium dioxide is manufactured by two processes: the chloride process and the sulfate process. Only the chloride process produces PCDD/PCDF as incidental byproducts.

The chloride process begins with the conversion of titanium-bearing ore – rutile, which is 93% to 96% TiO<sub>2</sub>, and ilmenite, which may contain between 44% and 70% TiO<sub>2</sub> – into TiCl<sub>4</sub>. This conversion is carried out in a fluidized bed chlorinator in the presence of Cl<sub>2</sub> at a temperature of approximately 900°C, with the addition of petroleum coke as a reductant. The volatile TiCl<sub>4</sub>, along with other volatile metal chlorides, exits the chlorinator as overhead vapor. The non-volatile metal chlorides, unreacted coke and ore solids are removed from the gas stream and from the bottom of the chlorinator. TiCl<sub>4</sub> is separated from the gaseous product stream and purified by condensation and chemical treatment. Vent gases from the chlorinator are scrubbed using water and caustic solutions then vented to the air. The purified TiCl<sub>4</sub> is then oxidized to produce TiO<sub>2</sub> and Cl<sub>2</sub> that is driven off is recycled to the chlorinator. The pure TiO<sub>2</sub> is slurried and sent to the finishing process which includes milling, addition of inorganic and organic surface treatments, and/or spray drying of the product TiO<sub>2</sub>. The product can be sold as a packaged dry solid or water-based slurry.

Typical wastes generated by the chloride process includes wastewaters from chlorinator coke and ore solids recovery, reaction scrubbers, chemical tank storage scrubbers, product finishing operations and wastewater treatment solids decantation. Waste sands from finishing (milling) of the TiO<sub>2</sub> product, scouring of oxidation process units, and blasting of reactor internal surfaces prior to replacement of refractory are also generated.

PCDD/PCDF were detected at concentrations of 0.010 and 0.020 pg TEQ/L in treated wastewater from two TiCl<sub>4</sub>/TiO<sub>2</sub> production facilities (USEPA 2006c). However, source reduction efforts have dramatically



reduced generation of PCDD/PCDF as reflected in the trend of TRI reports by the USEPA. By 2010 values of 0.0012 to 0.1771  $\mu\text{g TEQ/t}$  of product were representative.

PCDD/PCDF concentrations in residues from  $\text{TiCl}_4/\text{TiO}_2$  production facilities were reported as follows: wastewater treatment solids, 402 ng TEQ/kg; chloride solids/waste acid, 812 ng TEQ/L; filter press solids, 2,615 ng TEQ/kg (USEPA 2001). By 2010 PCDD/PCDF in solid residues had been reduced to a range of 8 to 42  $\mu\text{g TEQ/t}$  of product (USEPA 2010b).

In the U.S., a  $\text{TiCl}_4/\text{TiO}_2$  production facility has been identified as a possible source of PCDD/PCDF in sediments and shellfish of St. Louis Bay, Mississippi (Elston *et al.* 2005a, 2005b).

### Emission Factors

No data were available to allow derivation of an  $\text{EF}_{\text{Air}}$  for PCDD/PCDF releases from  $\text{TiCl}_4/\text{TiO}_2$  production.

**$\text{EF}_{\text{Water}}$ :** Values range from .0012 to .1771  $\mu\text{g TEQ/t}$  of product based on 2010 TRI data reported by USEPA and production data from TZ Minerals International.

**$\text{EF}_{\text{Product}}$ :** ND.

**$\text{EF}_{\text{Residue}}$ :** Based on 2010 TRI data reported by USEPA and production data from TZ Minerals International current solid residues range from 8 to 42  $\mu\text{g TEQ/t}$  of product.

### Caprolactam (2-Azacycloheptanone)

For PCDD/PCDF, an  $\text{EF}_{\text{Air}}$  of 0.00035  $\mu\text{g I-TEQ/t}$  of caprolactam and, for HCB and PCB,  $\text{EF}_{\text{Air}}$  of 3.2 and 8.1  $\mu\text{g I-TEQ/t}$ , respectively, have been derived by Iwata *et al.* (2008).

PCDD/PCDF concentrations as high as 680 pg I-TEQ/L were measured in untreated process wastewater from a caprolactam production facility in Japan and a concentration of 1.6 pg I-TEQ/L was found in the facility's treated combined wastewater (Kawamoto 2002). Lee *et al.* (2009) reported a PCDD/PCDF concentration of 0.045 pg I-TEQ/L in treated wastewater from a facility in Taiwan and derived an  $\text{EF}_{\text{Water}}$  of 0.936 ng I-TEQ/t of caprolactam. The findings of both studies suggest that PCDD/PCDF may also occur in wastewater treatment residues. PCDD/PCDF have also been identified in air emissions from caprolactam facilities in China (Hong and Xu 2012). However, information is not available to derive emission factors for releases to land, product and residue.

Due to the 35-fold disparity in the two values obtained for PCDD/PCDF concentrations in treated wastewater from caprolactam, no  $\text{EF}_{\text{Water}}$  is presented. Instead, the approximate mid-point of the two values, 0.50 pg TEQ/L can be used in conjunction with wastewater discharge rates to estimate PCDD/PCDF releases to water.

**$\text{EF}_{\text{Air}}$ :** An  $\text{EF}_{\text{Air}}$  0.00035  $\mu\text{g TEQ/t}$  of caprolactam has been derived by Iwata *et al.* (2008).

**$\text{EF}_{\text{Water}}$ :** In lieu of an  $\text{EF}_{\text{Water}}$ , a PCDD/PCDF concentration of 0.50 pg TEQ/L can be used to estimate PCDD/PCDF releases to water.

An HCB air emission factor of 3.2  $\mu\text{g TEQ/t}$  of caprolactam and PCB air emission factor of 8.1  $\mu\text{g TEQ/t}$  have been derived by Iwata *et al.* (2008).



## Annex 49 Complementary information to source category 7f Petroleum Industry

Oil refineries are large scale plants, processing about a hundred thousand to several hundred thousand barrels of crude oil a day. There are 655 refineries worldwide, located in 116 countries that collectively have a daily capacity of about 88 million barrels per day (b/d).<sup>27</sup> Because of the high capacity, many of the units operate continuously, as opposed to processing in batches, at steady state or nearly steady state for months to years. There are three broad categories of refining processes:

1. Separation: The oil is separated into its constituents by distillation, and some of these components (such as the refinery gas) are further separated with chemical reactions and by using solvents that dissolve one component of a mixture significantly better than another.
2. Conversion: The various hydrocarbons produced are then chemically altered to make them more suitable for their intended purpose. Prior to conversion, sulfur must be removed from the hydrocarbons because these reactions often require catalysts that are deactivated by sulfur.
3. Purification: The hydrogen sulfide gas that was extracted from the refinery gas is converted to sulfur, which is sold in liquid form to fertiliser manufacturers.

Detailed descriptions of refinery processes can be found in the European Commission's Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries (EC 2003).

### Release to Air

For catalytic reforming units, off-gas was reported to have a PCDD/PCDF concentration of 131 ng I-TEQ/Nm<sup>3</sup> (Jansson 1999). The California Air Resources Board (1999) determined an EF<sub>Air</sub> 3.04 ng TEQ/barrel for the catalytic reforming unit at one U.S. refinery. Both CONCAWE (2009) and U.S. EPA (2006a) derived an EF<sub>Air</sub> of 1.52 ng TEQ/barrel for these units. It is important to note that U.S. EPA (2004) reports that some refineries vent off-gases from these units directly to the air.

For refinery coking units, RTI (2011) derived an EF<sub>Air</sub> of 56.2 ng TEQ/barrel (353.5 ng/m<sup>3</sup> oil).

For flares at Danish refineries, Henricksen *et al.* (2006) derived an EF<sub>Air</sub> of 0.25 µg TEQ/TJ of fuel.

EF<sub>Air</sub> of 2.28 ng TEQ/barrel (0.0143 µg TEQ/m<sup>3</sup> oil; 0.0168 µg TEQ/t oil)<sup>28</sup> for catalytic reforming unit catalyst regenerators, based on the mid-point of the values presented by CARB (1999), CONCAWE (2009) and U.S. EPA (2005a).

EF<sub>Air</sub> of 56.2 ng TEQ/barrel (0.353 µg TEQ/m<sup>3</sup> oil; 0.413 µg TEQ/t oil) for refinery coking units, based on the value derived by RTI (2011).

EF<sub>Air</sub> of 0.25 µg TEQ/TJ of fuel for flares at oil refineries, based on value presented by Henricksen *et al.* (2006).

<sup>27</sup> Petroleum Online. Overview. <http://www.petroleumonline.com/content/overview.asp?mod=8>

<sup>28</sup> 1 barrel of oil = 0.159 m<sup>3</sup> of oil; 1 barrel of oil = 0.136 tons of oil.

### Release to Water

Data obtained from four U.S. refineries found PCDD/PCDF concentrations ranging from 0 to 394,000 pg TEQ/L, with a median of 2,975 pg TEQ/L in wastewater from their catalytic reforming units (USEPA 2004). The data also include PCDD/PCDF concentrations ranging from 0 to 37.9 pg TEQ/L, with a mean of 3.5 pg TEQ/L, in the final effluent of nine refineries. At one refinery, stormwater run-off was identified as the source of 50% of PCDD/PCDF in the final effluent with coke pond and clean canal forebay as the source of 45%. Karras (1998) reported a PCDD/PCDF concentration of 7.86 pg TEQ/L in the wastewater effluent of a U.S. refinery.

**EF<sub>Water</sub>** of 5 pg TEQ/L, based on the value presented by Karras (1998) and the mean of the values reported by U.S. EPA (2004).

### Release in Residues

Data describing PCDD/PCDF concentrations in the final wastewater treatment sludge of refineries were not available. However, PCDD/PCDF concentrations ranging from 3 to 356 ng TEQ/kg, with a median of 13.61 ng TEQ/kg were measured in sludge generated by oil and solids removal (API) separators at catalytic reforming units (USEPA 2004).

Refinery boilers and process heaters may produce fly ash and bottom ash as residues, but there is no information on their PCDD/PCDF content, generation rates and fate (see also Source Group 3). Spent catalyst generated is around 20-25 tons per year for a 5-million-tons-per-year refinery. Spent catalyst is typically regenerated and catalyst fines from that process are likely to be captured by abatement systems. With dry abatement systems, the catalyst fines become a discrete residue; if wet, the fines accumulate in wastewater treatment sludge.

**EF<sub>Residue</sub>** of 13.61 ng TEQ/kg for sludge from API separator of catalytic reforming unit, based on value determined by U.S. EPA (2004).

## Annex 50 Complementary information to source category 7g Textile Production

Of the 635,000 metric tons of dyes produced annually worldwide, about 10-15% of the dye is disposed of in effluents from dyeing operations. However, dyes in wastewater may be chemically bound to fabric fibers. The average wastewater generation from a large, centralized industrial U.S. dyeing facility is estimated at between 3.8 and 7.5 million liters per day (one and two million gallons per day). Dyeing and rinsing processes for disperse dyeing generate about 100-140 L of wastewater per kg of product (12-17 gallons of wastewater per pound). Similar processes for reactive and direct dyeing generate even more wastewater, about 125-170 L of wastewater per kg of product (15-20 gallons per pound of product) (USEPA 1997).

Based on the analyses of 16 samples from Germany, it was concluded that, the PCDD/PCDF concentration will not increase significantly during these finishing processes: mean concentrations found in finished cotton were at  $0.21 \pm 0.10$  ng I-TEQ/kg with a median of 0.20 ng I-TEQ/kg (Horstmann 1994). These results were confirmed by random sample analyses of raw and pre-treated cotton arriving at the Hamburg harbor, which contained 0.03-0.2 ng I-TEQ/kg (Hutzinger *et al.* 1995).

Whereas there are many data for PCDD/PCDF concentrations in final products (textiles), there are no data for residues and wastewater. Therefore, emission factors can be given only as upper bound and lower bound limits for the final product.

### Release to Air

In the only study of PCDD/PCDF air emissions from textile production processes that could be found, the following five processes were investigated (Sedlak *et al.* 1998):

- Crosslinker finish with  $MgCl_2$ , as catalyst;
- Flame retardant finish on fleece on the basis of  $Sb_2O_3$ /Hexabromocyclododecane;
- Flame retardant finish on upholstery material on the basis of ammonium bromide;
- Flame retardant finish on fleece on the basis of ammonium bromide; and
- Flame retardant finish on upholstery material on the basis of PVC,  $Sb_2O_3$ , hexabromocyclododecane.

PCDD/PCDF concentrations in air emissions from these processes were low, ranging from 1.7 to 2.6 pg TEQ/m<sup>3</sup>. However, relatively high concentrations of PXDD/PXDF were found in associated textiles and in chimney deposits. Data are not sufficient to derive emission factors.

### Release to Water

Only one study was found in which the PCDD/PCDF content of textile production wastewater was determined. In this study, a PCDD/PCDF concentration of 0.44 ng TEQ/L was measured in wastewater from a Slovenian textile-dyeing facility engaged primarily in wet-process dyeing of polyester yarns with disperse dyes (Marechal *et al.* 2012). Data are not sufficient to derive emission factors.

### Release in Products

Whereas in most samples of raw textiles, concentrations below 1 ng I-TEQ/kg were detected (means around 0.2 ng I-TEQ/kg), highly contaminated samples were also found. For example, 244 ng I-TEQ/kg were detected in bleached polyester, 370 ng I-TEQ/kg in blue cotton (Horstmann 1994), and 86 ng I-TEQ/kg in wool (Mayer 1997). The homologue profiles of all highly contaminated samples were dominated by the higher chlorinated PCDD and PCDF (Cl<sub>7</sub> and Cl<sub>8</sub>), which are indicators for PCP or chloranil-based dyes and pigments as the source of the contamination. However, several analyses confirmed that there is no correlation between PCP and PCDD/PCDF concentrations in textiles although the congener patterns gave strong indications that PCP should be the source. These findings make sense as PCP is water-soluble and will be removed in the finishing process and final washing processes whereas the PCDD/PCDF adsorb to the fiber and will stay in the textile (Horstmann and McLachlan 1995b, Klasmeier and McLachlan 1997).

The problem of PCDD/PCDF contamination of textiles is not yet resolved, as evidenced by a recent Swedish study that found textiles and leather to account for 90-95% of total PCDD/PCDF in source-separated combustible domestic waste (Hedman *et al.* 2007).

**EF<sub>Product</sub>** of 100 µg TEQ/t is presented as a reasonable upper limit value, based on values reported in existing studies.

**EF<sub>Product</sub>** of 0.1µg TEQ/t is presented as a reasonable lower limit value, based on values reported in existing studies.

**EF<sub>Product</sub>** of NA for textiles manufactured without formation or transfer of PCDD/PCDF (BAT Technology).

### Release in Residues

PCDD/PCDF have been reported in textile mill sludge (Wright 1996). However, data were not sufficient for the derivation of an **EF<sub>Residue</sub>**. The occurrence of PCDD/PCDF occur in wastewater treatment sludge from textile mills that use PCDD/PCDF-contaminated dyes and biocides is supported by the presence of PCDD/PCDF in the wastewater of such facilities, as reported by Marechal *et al.* (2012).

## Annex 51 Complementary information to source category 7h Leather Refining

Solid wastes generated by the leather can be classified as follows:

- Wastes from untanned hides/skins (trimmings, fleshing wastes);
- Wastes from tanned leather (shaving wastes, buffing dust); and
- Wastes from dyed and finished leather (trimmings from leather).

In addition to carrying chemicals directly required for or generated by leather production processes, leather production wastes also contain chemicals that are incidental to those processes, such as biocides. For example, in the analysis of eleven organochlorine biocides in raw hides from Europe, America and ten Africa countries, none were found in the European and American hides but one or more were found in 63% of the African hides (Font and Marsal 1998). Indeed, lindane and its residues were found in 56% of the African samples, with concentrations as high as 258 mg/kg. It is evident, however, that other organochlorines occur in European leather production. For example, three different chlorophenols, some at concentrations as high as 500 mg/kg, were measured in “wet blue” leather samples from Italy (Favaro *et al.* 2008). HCB was detected at a concentration of 3.3 µg/L in a composite sample of wastewater discharged from 100 small and big leather industrial units in India (Kumar *et al.* 2008). These three studies suggest that organochlorines may be common, if not ubiquitous, contaminants in the wastewater, wastewater treatment sludge and other solid wastes of leather production.

Leather wastes have high calorific values (4500-5000 kcal/kg). However, they also have salt content as high as 2.5% (Ozgunay *et al.* 2007), and, as indicated earlier, potentially significant levels of organochlorine chemicals. Both sources of chlorine – salt and organochlorine chemicals – may exacerbate PCDD/PCDF formation and release if such wastes are incinerated. For example, combustion of footwear leather waste in a semi-pilot scale incinerator was accompanied by PCDD/PCDF concentrations of 0.841 and 0.355 ng TEQ/Nm<sup>3</sup> in the flue gas (Godinho *et al.* 2009).

In contrast to textiles, once PCDD/PCDF-contaminated PCP is applied to leather, neither PCDD/PCDF nor PCP is easily removed by washing processes. In leather “breast-wallets” concentrations of PCDD/PCDF up to 430 ng I-TEQ/kg, in leather shoes up to 6,400 ng I-TEQ/kg were found (Malisch 1994). Although in many countries, the use of PCP has decreased, at least in shoes, the PCDD/PCDF concentrations did not decrease and in Germany, peak concentrations of 2,100 and 3,000 ng I-TEQ/kg were detected in leather shoes bought in 1991. In the year 1996, highly elevated concentrations continued to exist (Klasmeier and McLachlan 1997). For leather goods, the PCP concentrations correlate with PCDD/PCDF concentrations at least qualitatively. The homologue and congener profiles and patterns strongly indicate that PCP is the source of the dioxin contamination.

The continued use of PCP is evidenced by a case in Germany in which a PCP concentration of >2000 mg/kg was found in a leather jacket, following the discovery of high PCP levels in the plasma of a child and her parents (Heudorf *et al.* 2003). In 2007, Hedman *et al.* (2007) found that leather and textiles accounted for 90-95% of total PCDD/PCDF in source-separated combustible domestic waste in Sweden.

A more detailed discussion of leather production processes can be found in the BAT&BEP Guidelines.

### **Emission Factors**

Emission factors for PCDD/PCDF releases to air, water, land, and residues could not be derived due to lack of information. However, it is important to note, to the extent possible, the quantities, methods of treatment, and fate of wastewater, treated wastewater effluents, wastewater treatment sludge, and other solid wastes since PCDD/PCDF releases to water and residues could be high. If wastewater treatment sludge and/or other wastes are applied to land or incinerated or otherwise combusted, this should also be noted since release to air, land and in residues could be high.

**EF<sub>Product</sub>** of 1,000 µg TEQ/t is presented as a reasonable upper limit value, based on values reported in existing studies.

**EF<sub>Product</sub>** of 10 µg TEQ/t is presented as a reasonable lower limit value, based on values reported in existing studies.

## Annex 52 Complementary information to source group 8 Miscellaneous

### Overview of recent revisions

New emission factors are included for residues in category 8a Dying of biomass and 8e Tobacco smoking. In category 8b Crematoria, open air cremations have been explicitly introduced in class 2.

### Derivation of emission factors

#### 8a Drying of Biomass

##### Release to Air

Measured concentrations in air ranged from 0.005 ng I-TEQ/Nm<sup>3</sup> to 3.51 ng I-TEQ/Nm<sup>3</sup> with a median of 0.16 ng I-TEQ/Nm<sup>3</sup> (LUA 1997). The very high concentration was found when PCP-treated wood was used as a fuel for drying of green fodder.

##### Release in Products

Concentrations in the product, *e.g.*, virgin wood are close to detection limit, around 0.1 ng I-TEQ/kg and for fodder, concentrations as being found in biomonitoring studies with Welsh rye grass can be used. The concentrations found in the dried product, when contaminated wood was used as a fuel, were between 0.3 and 0.8 ng I-TEQ/kg d.m. An emission factor of 0.5 µg I-TEQ/t should be applied if PCP-treated wood is the fuel and an emission factor of 0.1 µg I-TEQ/t will be applied if clean fuel is used (LUA 1997).

##### Release to Residues

Emission factors for residues have been developed based on expert judgment and analogy with category 8c Smoke houses.

#### 8b Crematoria

##### Release to Air

Kim *et al.* (2003) reported air emissions from 0.46 to 2.1 ng TEQ/Nm<sup>3</sup> from Korean crematoria corresponding to an emission factor of 8.4 µg TEQ/body cremated.

In Thailand, PCDD/PCDF concentrations were measured in flue gas and bottom ashes from a crematory that had a refractory-lined primary combustion chamber and a secondary combustion chamber with an afterburner. Both chambers were fired with light fuel-oil. Flue gases were directed through a refractory-lined flue gas duct that discharged through an underground brick flue gas duct into a brick-lined stack located about 15 meters away from the furnace (UNEP 2001, Fiedler *et al.* 2002).

Since the Thai crematory had an afterburner, it would have been considered as class 2 with an EF<sub>AIR</sub> of 10 µg TEQ/body cremated. However, PCDD/PCDF concentrations at the stack ranged from 10.5 to 28.6 ng I-TEQ/m<sup>3</sup> with an average of 17.6 ng I-TEQ/m<sup>3</sup> (at 11% O<sub>2</sub>). The EF<sub>AIR</sub> derived from this value is 18 µg TEQ/body cremated, which is higher than that for class 2 crematories. This is attributed to the discharge of combustion gases through a long underground flue gas duct, which maintained the gases at temperatures favoring PCDD/PCDF formation (UNEP 2001, Fiedler *et al.* 2002).

A national monitoring program of air pollutant releases from crematoria, including PCDD/PCDF, was carried out in France in 2005 (Livolsi *et al.* 2011). Results show that:

- PCDD/PCDF concentrations in flue gas generally ranged from 0.1 to less than 1 ng I-TEQ/m<sup>3</sup>. However, a high concentration of 4.18 ng I-TEQ/m<sup>3</sup> was found at one crematorium. This exceptional ly high emission could not be explained.
- For crematoria, PCDD/PCDF concentrations in flue gas are higher than the air emission limit value for municipal solid waste incinerators (0.1 ng I-TEQ/Nm<sup>3</sup>).

Factors that influence dioxin emissions from crematoria could not be identified.

### **Release to Water**

Normally, wet scrubbers or water quenching are not used at crematoria and thus, no discharges to water will occur. If wet scrubbers are used, the wastewater may end up in local sewer systems or be discharged without any prior treatment. In Western Europe, APC systems are commonly wastewater-free because the wastewater is evaporated internally.

### **Release to Land**

There are no releases to land.

### **Release in Products**

There are no products generated.

### **Release in Residues**

Poor combustion conditions will result in poor burn-out of the organic carbon and in higher concentrations in the fly ash and furnace ash. PCDD/PCDF concentrations in the bottom ashes collected from a crematory in Thailand were 44 and 48 ng I-TEQ/kg of bottom ash (UNEP 2001, Fiedler *et al.* 2002). However, insufficient data are available to provide an emission factor.

## **8c Smoke Houses**

### **Release to Air**

PCDD/PCDF concentrations in off-gases from smoke houses have been published from Germany (LAI 1995). A conventional smoke-curing chamber emits about 300 m<sup>3</sup>/h of flue gas and produces about 50 kg product per hour. The flue gas volume will be 6,000 m<sup>3</sup>/t product. With the measured data of 1.02 ng TEQ/m<sup>3</sup> for a smoke house without thermal afterburning and 0.1 ng TEQ/m<sup>3</sup> for a smoke house with thermal afterburning, the emission factors for class 2 and class 3 have been derived.

### **Release to Water**

Normally, wet scrubbers are not used at smoke houses and thus, no discharges to water will occur.

### **Release to Land**

There are no releases to land.

### **Release in Products**



There are no systematic measurements on smoked meat and fish. An increase in the dioxin concentration of the foodstuff has been found in a few measurements. However, the concentration in the foodstuff is determined by the origin of the foodstuff (with higher concentrations in beef and sheep, lower concentrations in pork; highly variable with eventually very high concentrations in fish).

### **Release in Residues**

The emission factors are the same as those for wood combustion.

## **8d Dry Cleaning**

### **Release to Water**

No release to water is expected.

### **Release to Land**

No release to land is expected.

### **Release in Products**

There are no products generated (concern is with the distillation residues only).

### **Release in Residues**

Emission factors for residues are derived for highly contaminated textiles (3,000 µg TEQ/t distillation residue) and normal textiles (50 µg TEQ/t distillation residue) based on Towara *et al.* (1992) and Umlauf *et al.* (1993).

## **8e Tobacco Smoking**

Investigations of the ten most popular brands smoked in Germany gave “emissions” of 0.1 pg I-TEQ/cigarette (Ball *et al.* 1990). In Japan, Aoyama *et al.* (2003) reported PCDD/PCDF in mainstream and sidestream cigarette smoke at concentrations of 0.35 to 2.4 pg TEQ per cigarette for five popular brands. In evaluating PCDD/PCDF in mainstream smoke from U.S. cigarettes, Wilson *et al.* (2008) reported concentrations of 5.8-28.4 fg TEQ/cigarette for low-tar cigarettes, 18.7 to 162.6 fg TEQ/cigarette for medium-tar cigarettes, and 61.0-181.5 fg TEQ/cigarette for high-tar cigarettes. Including all cigarette grades, the average PCDD/PCDF content of mainstream smoke was 69.1 fg TEQ/cigarette.

### **Release to Air**

An  $EF_{Air}$  of 1 pg TEQ/cigarette is presented based on Ball *et al.* (1990) and Wilson *et al.* (2008).

An  $EF_{Air}$  of 3 pg TEQ/cigar is presented based on the assumption that the quantity of tobacco in an average cigar is about three times that of a cigarette.

### **Release to Water**

$EF_{Water}$  is set to NA.

### **Release to Land**

$EF_{Land}$  is set to NA.

### **Release in Products**

There are no products generated.

### **Release in Residues**

An  $EF_{\text{Residue}}$  of 0.1  $\mu\text{g TEQ/million cigarettes}$  is presented based on Aoyama *et al.* (2003).

An  $EF_{\text{Residue}}$  of 0.3  $\mu\text{g TEQ/million cigars}$  is presented based on the assumption that the amount of ash in an average cigar is about three times that of a cigarette.

## Annex 53 Complementary information to source group 9 Disposal / Landfill

### Overview of recent revisions

Emission factors were revised for source categories 9a Landfills, Waste Dumps and Landfill Mining, 9b Sewage and Sewage Treatment and 9d Composting. The information used to revise the emission factors is presented below, in the respective sections.

### Derivation of emission factors

#### 9a Landfills, Waste Dumps and Landfill Mining

##### Release to Air

On average, 1 ton of normal municipal waste in a landfill generates 150 m<sup>3</sup> of landfill gas (European waste) during a period of 10-20 years (or even longer). The highest gas production normally takes place in the early years after disposal. Measurements of landfill gas have not produced any quantifiable PCDD/PCDF concentrations. However, PCDD/PCDF have been detected in flares and exhausts of gas-fired motors (see source category 3c Landfill and Biogas Combustion). No measurable PCDD/PCDF release to air is expected from this activity.

##### Release to Water

The leachate or seepage from landfills and dumps can contain PCDD/PCDF. From a Korean industrial waste landfill, Jin *et al.* (2007) reported a PCDD/PCDF concentration range of 0-31.17 µg TEQ/m<sup>3</sup> in a leachate sample described as “water”, indicating analysis of the aqueous phase. In the U.S., Litten *et al.*, (2003) reported an average PCDD/PCDF concentration of 0.32 pg/L in treated landfill leachate, which were analyzed in conjunction with numerous other aqueous samples. Hiraoka *et al.* (1993) found PCDD/PCDF concentrations ranging from 0.076 to 6.3 ng/l (> 0.05 ng TEQ/L) in landfill leachates that had undergone biological treatment, coagulation and sedimentation, sand filtration, and/or activated carbon adsorption. In a Spanish study leachate from eight different landfills contained 1.6- 1520 pg I- TEQ/L (Casanova *et al.* 1994).

PCDD/PCDF are likely to be concentrated in any oily phase of the leachate (the oily phase can be found either above or below the aqueous phase). However, the solubility of PCDD/PCDF in water is enhanced by the presence of detergents, other surfactants and dissolved humic acids (Yoshikawa *et al.* 1999, Nishikawa *et al.* 1999, Schramm *et al.* 1995, Kim and Lee 2002).

Data from five landfills in New Zealand ranged from 7.5 to 221 pg I-TEQ/L. The New Zealand inventory subdivided the range into 14-48.3 pg I-TEQ/L for small and medium landfills and 7.5-221 pg I-TEQ/L for large landfills (New Zealand 2000). The highest concentration came from a landfill with significant portions of industrial and potentially hazardous wastes.

For the Toolkit, the releases via leachates from the deposited waste for the inventory year is calculated and the estimated content for the respective class.

Three classes are suggested: class 1 with an emission factor of 5  $\mu$  TEQ/t waste for landfills which contains industrial wastes from category 1 to 8, class 2 with an emission factor of 0.5  $\mu$ g TEQ/t for landfills which may contain hazardous wastes and class 3, with an emission factor of 0.05  $\mu$ g TEQ/t for landfills containing non-hazardous municipal wastes.

### Release to Land

Contamination of land can result from poorly controlled dumps and landfills.

### Release in Products

There is no product.

### Release in Residues

There is no residue. However, with the presence of PCDD/PCDF, landfills may serve as a reservoir and a potential source in the future. PCDD/PCDF concentrations in municipal solid waste<sup>29</sup> have been reported to range from less than 1 ng I-TEQ/kg to levels of 100 ng I-TEQ/kg, and peak concentrations several orders of magnitude higher (especially when dust fractions are present). In Germany, a mean concentration of 50 ng I-TEQ/kg was estimated from wastes sampled in the late 1980s (Wilken *et al.* 1992). In the UK, a mean concentration of 6 ng I-TEQ/kg was measured in the mid 1990s. In a recent study in Italy, PCDD/PCDF concentrations in MSW were ranging from 1.6 to 44 ng TEQ/kg (Grosso *et al.* 2012).

Since it is anticipated that hazardous waste is being generated within the productive sector and is being accounted therein as residue, the  $EF_{Residue}$  is set to “not applicable” for class 9a. For classes 9b and 9c, the amount (in tons of solid waste) disposed of within the reference calendar year constitutes the activity for “residue”.

When landfills are excavated for mining purpose or due to remediation measures, the deposited PCDD/PCDF can become a relevant source if PCDD/PCDF contaminated wastes have been deposited (see source group 10). The amount of PCDD/PCDF present in landfills or waste dumps will be determined by the level of PCDD/PCDF sources in the country. For landfills having received specific wastes in the past, especially from the organochlorine industry or industries using elemental chlorine, site-specific PCDD/PCDF inventories need to be compiled (see source group 10).

## 9b Sewage and Sewage Treatment

### Release to Air

There are almost no data describing PCDD/PCDF releases to air from sewage treatment facilities.

### Release to Water

Because PCDD/PCDF have very low solubility in water, treated effluents from sewage treatment facilities are expected also to be very low. However, the solubility of PCDD/PCDF in water is enhanced by the presence of detergents, other surfactants and dissolved humic acids (Yoshikawa *et al.* 1999, Nishikawa

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<sup>29</sup> It should be kept in mind that it is very difficult or almost impossible to take a representative waste sample and determine its PCDD/PCDF concentration.

*et al.* 1999, Schramm *et al.* 1995, Kim and Lee 2002), all of these being commonly present in domestic and municipal wastewater. In addition, the use of chlorine for disinfection of treated effluents can increase PCDD/PCDF concentrations by as much as 50-fold: a PCDD/PCDF concentration of 0.006 pg TEQ/L was measured in treated effluent that had not been subject to chlorine disinfection, while a PCDD/PCDF content of 0.3 pg TEQ/L was determined in treated effluent that had undergone chlorine disinfection (Pujadas *et al.* 2001).

### Release to Land

Sludge from sewage treatment may be applied to land to improve soil quality and as a management approach for sewage sludge. If so, the  $EF_{\text{Product}}$  will be used for the  $EF_{\text{Land}}$ .

### Release in Products

Sludge may be considered a product when it is applied to land as a soil improvement or is marketed for such use. In these cases it will be considered a release to land. Sludge otherwise disposed of will be accounted for as a release in residues.

Here, sewage sludge is the product and there is no residue generated.

### Release in Residues

PCDD/PCDF concentrations in sewage sludge have been measured since the late 1980s, when Hagenmaier found an average concentration of 200 ng TEQ/kg d.m. from 43 German sewage sludge treatment plants (Hagenmaier 1988). Subsequently, about 300 plants were analyzed to give an average of 50-60 ng TEQ/kg d.m. (Butzkamm-Erker and Mach 1990). In 30 Swiss sewage plants, Rappe *et al.* (1994) found concentrations between 6 and 4,100 ng I-TEQ/kg d.m., with four samples above 1,000 ng I-TEQ/kg d.m. During the last 25 years, the values of PCDD/PCDF have decreased considerably. Today, the average PCDD/PCDF values in Swiss sewage treatment plants are around 10 ng TEQ/kg (M. Zennegg, personal communication, 20 February 2012) and in Swedish sewage sludge below 3 ng I-TEQ/kg d.m. (Swedish Environmental Ministry 2010). These values are similar to the recent review of PCDD/PCDF levels in sewage sludge in Australia, registering a mean value of 6 ng I-TEQ/kg with most sludge samples around 2 and 3 ng I-TEQ and a two sludge samples between 10 and 20 ng TEQ/kg. In the Australian study, only a minor difference between the average for urban sludge (7 ng TEQ/kg) and rural sludge (5 ng TEQ/kg) was found (Clarke *et al.* 2008). In a Chinese survey, four sludge samples were between 3 and 7 ng TEQ/kg with two sludges at 33 and 88 ng TEQ/kg (Dai *et al.* 2007). In a Spanish survey, 24 of 31 samples collected were below 20 ng TEQ/kg, with only one sludge from an industrial area impacted by textile industries having relatively high levels (346 ng TEQ/kg) (Fuente *et al.* 2007).

Based on these data, the following emission factors are included in the Toolkit:

- 4 ng TEQ/kg for sewage treatment plants in remote areas and urban areas with only domestic inputs;
- 20 ng TEQ for sewage treatment plants in urban environment with mixed input from households and industry without specific potential to contain PCDD/PCDF;

- 200 ng TEQ/kg for sewage treatment plants with specific industrial impact with a potential to contain PCDD/PCDF as described for categories 1 to 8.

For the respective classes, emission factors are also given for releases into water depending if sludge is effectively removed or not in the respective plant.

## 9d Composting

### Release to Air

Emissions to air are very low (few pg per m<sup>3</sup>) and may be considered negligible.

### Release to Water

The composting process generates water, however, the concentrations are normally very low and the water is recycled into the compost during the process.

### Release to Land

The most common use of finished compost is application on land or marketing for that purpose, therefore the EF<sub>Product</sub> is the EF<sub>Land</sub>.

### Release in Products

In a comprehensive study in Europe, PCDD/PCDF levels were measured in 185 composts. Average PCDD/PCDF levels in these composts were below 10 ng TEQ/kg dw (Brändli *et al.* 2005). Concentrations varied to a limited extent between compost containing organic household waste (9.6 ng I-TEQ/kg dry wt., n = 124) and containing green waste (8.5 ng I-TEQ/kg dry wt., n = 61); the differences were not significant (Brändli *et al.* 2005). A more recent study in Switzerland detected lower levels at 3.2 ng TEQ/kg dw (Brändli *et al.* 2008).

The levels of PCDD/PCDF in organic compost (separated at source) in Brazil were on average of 14 ng TEQ/kg. However compost made from mixed wastes, where organic fractions have been separated after the collection of mixed wastes, had a higher average content of 57 ng TEQ/kg, with a maximum of 150 ng TEQ/kg in metropolitan areas; an average of 27 ng TEQ/kg was measured in small towns (Grossi *et al.* 1998). In addition, compost impacted by a pulp and paper sludge (Kraft process) had higher levels of 99 ng TEQ/kg (Grossi *et al.* 1998). Composts with PCDD/PCDF concentrations of 50 ng TEQ/kg and higher are not considered suitable for agriculture or horticulture.

An EF<sub>Product</sub> of 5 ng TEQ/kg d.w. should be applied for compost produced from clean organics (separated at source) or green waste.

An EF<sub>Product</sub> of 50 ng TEQ/kg should be applied for compost made from organics separated from mixed (household) waste “grey compost” or from industrial organic residues containing PCDD/PCDF<sup>30</sup>.

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<sup>30</sup> Organic residues from industrial processes with known relevant PCDD/PCDF emissions should not be used for composting purposes.

## Example Inventory 1 Updating and Revising an Inventory

### 1. Example of inventory updating and revision triggered by changes in emission factors

This example illustrates the inventory updating and revision for a single source class – open burning of domestic waste - which is triggered by the revision of the emission factor in the Toolkit methodology.

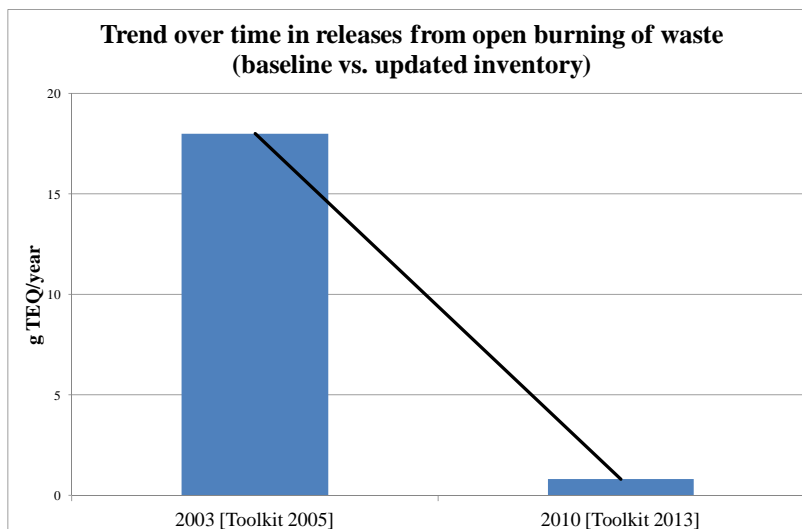
Let's consider a hypothetical inventory of country X. **The baseline inventory** is developed in 2005, based on data collected for the reference year 2003 and by using the Toolkit 2005 methodology. The baseline inventory estimates that approximately 60,000 tons of domestic waste from rural and urban areas is burned in 2003. The total annual releases of the baseline year are calculated based on the Toolkit 2005 methodology, by applying an emission factor for air of 300 µg TEQ/t of material burnt. The baseline releases to air from open burning of domestic waste are thus estimated at 18 g TEQ/year.

$$\begin{aligned} \text{Baseline PCDD/PCDF released to air in 2003 (g TEQ/year)} &= \text{Quantity of waste burnt} \times EF_{\text{Air}} \\ &= 60'000 \text{ t/yr} \times 300 \mu\text{g TEQ/t} \\ &= \underline{18 \text{ g TEQ/year}} \end{aligned}$$

Country X implements measures to reduce releases from open burning as part of the action plan within the National Implementation Plan, and initiates an update of the PCDD/PCDF inventory to assess the success of these measures and report them as part of the national report under Article 15.

**The updated inventory** is developed in 2013, based on data collected for the reference year 2010 and the Toolkit methodology as revised in 2013. 2010 activity rates for this source were assessed at around 20,000 tons of domestic waste burned annually. The corresponding emission factor was revised since the first inventory and is much lower than the one used for the baseline inventory:  $EF_{\text{Air}}$  is now 40 µg TEQ/t of material burned. The total annual releases are calculated based on the Toolkit 2013 methodology as below:

$$\begin{aligned} \text{Updated PCDD/PCDF released to air in 2010 (g TEQ/year)} &= \text{Quantity of waste burnt} \times EF_{\text{Air}} \\ &= 20'000 \text{ t/yr} \times 40 \mu\text{g TEQ/t} \\ &= \underline{0.8 \text{ g TEQ/year}} \end{aligned}$$



The total releases to air from open burning of domestic waste are thus estimated at 0.8 g TEQ/year in 2010. This translates into a significant reduction in releases to air from this source class from 2003 to 2010 (-95% decrease) as illustrated below:

This assessment is not correct as it does not consider that along with the decrease in the activity level

from 2003 to 2010, the emission factor has also been revised downwards. Since the basis for the calculation is not the same in the updated inventory as in the baseline **the estimations are not coherent** and the initial inventory will have to be reassessed to allow for correct trends over time to be calculated.

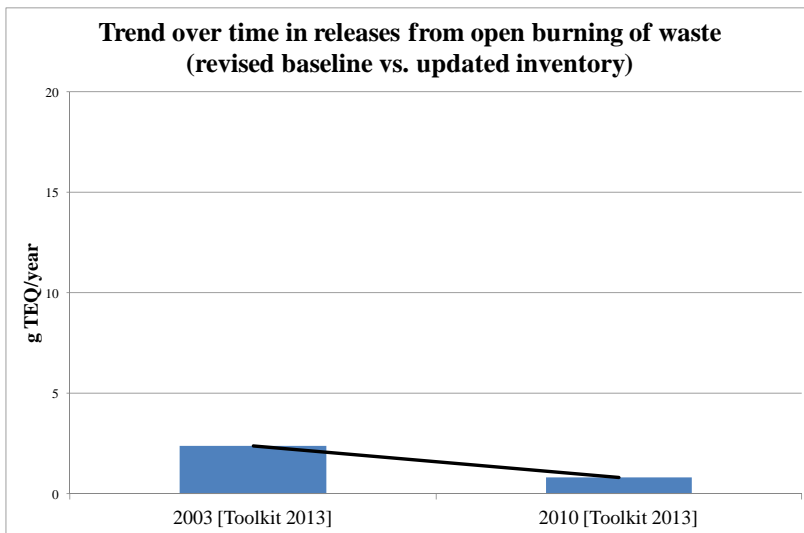
**The revised baseline estimate** will be the product of the baseline activity levels that were assessed for 2003 (60,000 tons of domestic waste burned per year) and the revised emission factors taken from the Toolkit 2013 methodology which was used in the updated inventory: 40 µg TEQ/t for air. The revised baseline levels of releases are thus 2.4 g TEQ/yr.

Revised PCDD/PCDF released to air in 2003 (g TEQ/year)=

Quantity of waste burnt x EF<sub>Air</sub>=

60'000 t/yr x 40 µg TEQ/t=

2.4 g TEQ/year



The revision of the baseline inventory allowed country X to assess correct trends over time and see that indeed there was a decrease in releases from 2003 to 2010, but this amounted to only 66%.

## 2. Example of inventory updating and revision triggered by an additional source class

Let's now consider another source category in this hypothetical inventory, where the revision of the baseline inventory is triggered by an additional class included in the revised Toolkit methodology.

**The initial/baseline inventory** was performed in 2005, based on 2003 data and the Toolkit 2005 methodology. In 2003, country X estimates that 4'000'000 tons of agricultural residues are burnt in poor conditions. An emission factor for air of 30 µg TEQ/t is applied according to the Toolkit 2005 methodology, and the overall emissions to air from this source class are estimated at 120 g TEQ/yr.

Baseline releases from agricultural residue burning in 2003 (g TEQ/year)=

Quantity of material burnt x EF<sub>Air</sub>=

4'000'000 t/yr x 30 µg TEQ/t= 120 g TEQ/year

In 2013 country X updates the inventory based on 2010 data and by using the 2013 revised version of the Toolkit. The emission factor for agricultural residue burning in poor conditions is the same as in the 2005 methodology: 30 µg TEQ/t. **The updated inventory** assesses the activity rate as 2'000'000 t material burnt annually. In addition, the developer of the inventory discovers that a new class was added to this source category, which is of major relevance for the country: this is sugarcane burning.



The new emission factor for sugarcane burning included in the 2013 methodology is of 4 µg TEQ/t, while the activity rate for this source class is estimated at 2'000'000 tons residues burnt annually. The release estimates are calculated as below, by multiplying the activity rate with the respective emission factors:

Updated releases from agricultural residue burning in 2010 (g TEQ/year)=

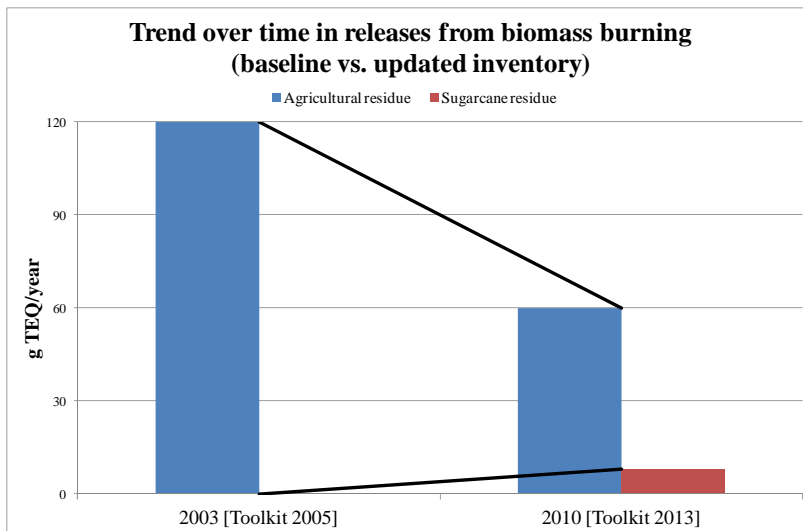
*Quantity of material burnt x EF<sub>Air</sub>=*

*2'000'000 t/yr x 30 µg TEQ/t= 60 g TEQ/year*

Updated releases from sugarcane burning in 2010 (g TEQ/year)=

*Quantity of material burnt x EF<sub>Air</sub>=*

*2'000'000 t/yr x 4 µg TEQ/t= 8 g TEQ/year*



Further to the updating of the inventory, the immediate conclusion would be a 50% reduction in air emissions from agricultural residue burning and a significant increase from 0 to 8 g TEQ in air emissions from sugarcane burning.

This conclusion is wrong, because the new class has to be assessed separately in the baseline inventory, similarly as in the

updated inventory. At the time the baseline inventory was developed, emission factors were not yet specifically developed and available to assess releases from sugarcane burning, and this source class had to be assessed together with other types of agricultural residues. There is a need to go back to the previous inventory and revise the calculations therein to include this new class. Only after this revision, the comparison between the situation in 2003 and the one in 2010 can be done.

In **the revised baseline inventory**, activity rates for the two source classes (agricultural residue burning and sugarcane burning) need to be retrospectively estimated for the baseline year. In 2003, from the initially estimated 4'000'000 t agricultural residues burnt annually, only 3'000'000 t actually corresponded to this source class; the remaining 1'000'000 tons were actually sugarcane residues that were burnt in the open. Therefore, in the baseline year, emissions to air from agricultural residue burning were of 90 g TEQ/yr, while the emissions from sugarcane burning were of 4 g per year.

Revised releases from agricultural residue burning in 2003 (g TEQ/year)=

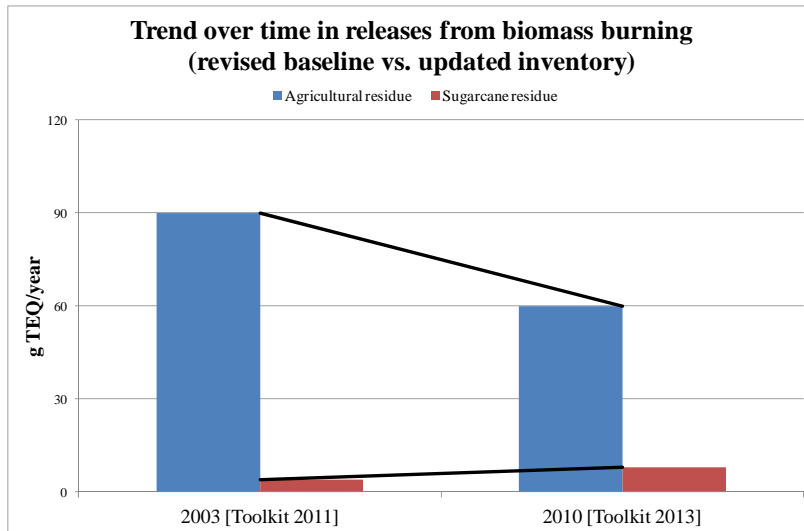
*Quantity of material burnt x EF<sub>Air</sub>=*

$$3'000'000 \text{ t/yr} \times 30 \mu\text{g TEQ/t} = \underline{90 \text{ g TEQ/year}}$$

$$\underline{\text{Revised releases from sugarcane burning in 2003 (g TEQ/year)=}}$$

$$\text{Quantity of material burnt} \times EF_{\text{Air}} =$$

$$1'000'000 \text{ t/yr} \times 4 \mu\text{g TEQ/t} = \underline{4 \text{ g TEQ/year}}$$



The revision of the baseline inventory shows that the actual reduction in air emissions from agricultural residue burning is of only 33%, while the increase in air emissions from sugarcane burning is only of 4 g TEQ:

### 3. Example of inventory updating and revision triggered by a missing source

This example illustrates a different type of situation, where the revision of the baseline inventory is not triggered by the changes in the methodology, but rather by better information becoming available at the country level during the inventory updating process.

We'll take the example of another source group: waste incineration.

**The baseline inventory** of country X mentions that the incineration of animal carcasses is rarely applied in the country and information for this source category is not available. It is thus considered that releases from this source category are negligible in 2003.

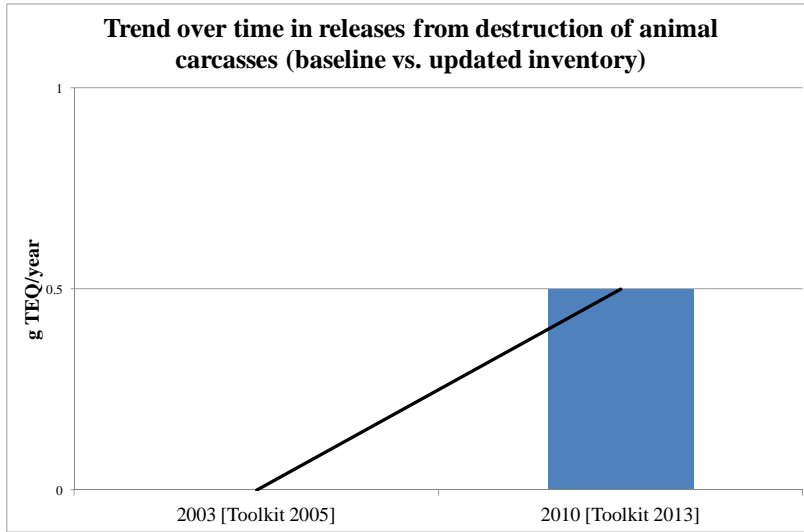
With the **updating of the inventory** in 2013, country X discovers that one old facility exists that is specialized in thermal destruction of carcasses. The activity rate for 2010 (the reference year in the updated inventory) is estimated at 1'000 t carcasses destroyed. The emission factor applied is of 500  $\mu\text{g TEQ/t}$ , corresponding to old facilities without air pollution control system. The overall emissions to air from this source category amount to 0,5 g TEQ/year.

$$\underline{\text{Updated PCDD/PCDF released to air in 2010 (g TEQ/year)=}}$$

$$\text{Quantity of carcasses} \times EF_{\text{Air}} =$$

$$1'000 \text{ t/yr} \times 500 \mu\text{g TEQ/t} =$$

$$\underline{0.5 \text{ g TEQ/year}}$$

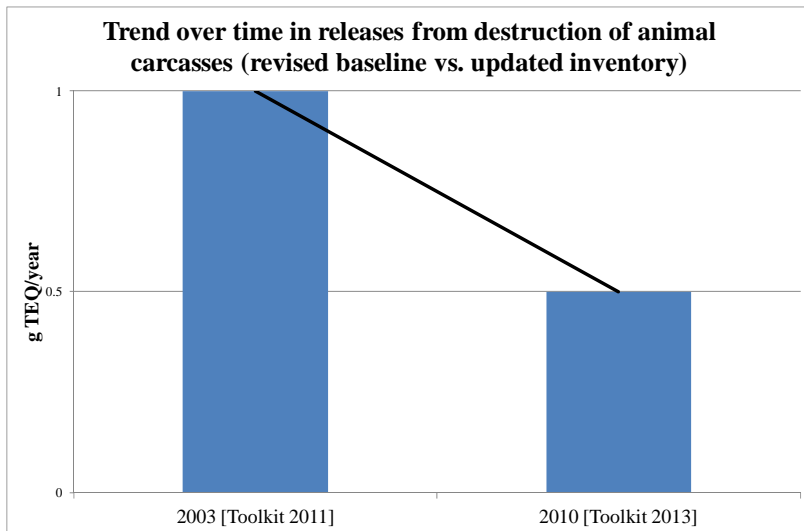


This would mean that an increase in emissions from this source took place from 2003 to 2010.

Nevertheless, the facility was operational in the baseline year as well, releasing dioxins and furans in the environment. A revision of the baseline inventory is thus necessary to ensure coherent trends over time. The revised baseline inventory estimates that the activity rate of this facility in 2003 was of 2'000 t of carcasses

destroyed, double the amount in 2010. The corresponding emission level is of 1 g TEQ/yr.

$$\begin{aligned} \text{Revised PCDD/PCDF released to air in 2003 (g TEQ/year)} &= \text{Quantity of carcasses} \times EF_{\text{Air}} \\ &= 2'000 \text{ t/yr} \times 500 \mu\text{g TEQ/t} \\ &= \underline{1 \text{ g TEQ/year}} \end{aligned}$$



The revision of the inventory enabled thus country X to observe an actual decrease in emissions from this category. If the revision was not performed, the incorrect conclusion would have been, on the opposite, an increase in emissions.

## **Example Inventory 2 Source Group 1 Waste Incineration**

### **I. Example of baseline inventory using national waste combustion statistics as a major activity data source**

This example illustrates the inventory process in the case where activity data are mainly obtained through national waste combustion statistics (questionnaires are partially used/targeted to obtain detailed information on incineration technologies in place). The example provides information on the baseline inventory process only, and is mainly focused to providing useful guidance on estimating activity rates.

Country X prepared its first inventory of dioxins and furans in 2006 to support the development of the action plan as required by Article 5 of the Convention. Activity data for the different sources of PCDD/PCDF were collected for the reference year 2004 (baseline year). The inventory is developed by applying the Toolkit 2005 methodology and the emission factors specified in that version of the Toolkit. Activity data was obtained from waste incineration national statistics.

According to waste statistics, in 2004 350,000 tons of wastes of more than 50 types were incinerated. Greatest incinerated volumes are communal-domestic wastes, wood wastes without pollution ('clean' wood wastes), polluted wood wastes, petrochemical sludge, wastes from paint production, waste petroleum oils, old tires, wastes from chipboard production, wastes from resins production, old sleepers impregnated with creosote, rags polluted with oils, old containers from pesticides, polluted paper and cardboard, liquid spirits, washing waters from chemical production and petroleum products storage, and hospital wastes.

For the quantification of PCDD/PCDF emissions, these major categories of combusted wastes were aggregated into different categories according to the Toolkit classification.

It was thus accounted that 60,000 tons of wastes are 'Municipal solid wastes', 50,000 tons 'Hazardous wastes', 5,000 tons 'Medical wastes', and 70,000 tons 'Waste wood and waste biomass'. No incineration of sewage sludge, light fraction shredder wastes and animal carcasses was accounted for.

Among these waste types, 10,000 tons of old tyres were combusted in cement kilns; PCDD/PCDF emissions from this category were accounted for in Group 4 – Mineral products. 100,000 tons of 'clean' wood wastes and 40,000 tons of biomass waste were incinerated in boilers for energy and heat production and accounted in Group 3. 15,000 tons of wastes could not be included into any category and PCDD/PCDF emissions from their incineration were not accounted for.

In addition, statistical data on wastes combusted in private households could not be obtained; an expert assessment of the total amount of such wastes used as an energy source for residential purposes was made, and emissions were accounted in Source Group 3.

The Environmental Protection Agency notifies that there are ten waste incineration plants in the country which mostly burn municipal wastes (or similar) and two plants which incinerate medical wastes. No statistical data could be found on the distribution of wastes according to the technology of combustion and level of abatement. To obtain such detailed data, questionnaires were sent to major

waste incineration facilities, communal services and companies which produce the largest amounts of wastes.

It was found that most of the industrial waste and partially medical wastes are incinerated 'on-site', by the plant/hospital generating these wastes. As for municipal wastes, these are incinerated at special plants.

Through the analysis of the questionnaires it was found that waste incineration practices include simple types of incineration furnaces, mostly batch-type. It was thus concluded that most of the waste combustion installations are equipped with simple abatement devices (1-stage with afterburners, cyclones, scrubbers), which correspond to Class 2 of the Toolkit. Only a minor part of incineration facilities are equipped with 2-stages abatement systems including bagfilters; this corresponds to Class 3 of the Toolkit. Finally, some facilities do not have abatement at all (Class 1).

There is no special management of residues from waste burning and fly ash: these are collected and landfilled together with other industrial and municipal wastes.

According to these data, baseline estimates of PCDD/PCDF emission from this source group amounted to:

- Air emission: 54.9 g/TEQ,
- Emission to residues: 58.6 g/TEQ

## **II. General example of baseline inventory, updating and revision**

### **Introduction**

The purpose of this case study is to illustrate the process of inventory development, update and revision, including the various triggering factors that may come into play in this process. We will consider a hypothetical example of an inventory of country X, and describe the baseline inventory process, its update and revision, focusing on a single source group: Waste Incineration.

### **Baseline inventory**

Country X prepares its first (baseline) inventory of dioxins and furans in 2006 to support the development of the action plan as required by Article 5 of the Convention and included in the National Implementation Plan pursuant to Article 7. Activity data for the different sources of dioxins and furans in country X are collected for the reference year 2004 (baseline year). The inventory is developed by applying the Toolkit 2005 methodology and the emission factors specified in that version of the Toolkit.

From the seven source categories included in this source group, only three are relevant for country X in the baseline year. These are presented below.

#### **1a Municipal Solid Waste Incinerators**

The preparer of the National Inventory sends a request to the national environmental permitting authority, asking for the number of MSW incinerators with active permits in 2004, their basic designs, design capacities and locations. The permitting authority reports that 30 MSW incinerators were permitted and active in country X during that year and provides the additional information requested for

each incinerator. Based on their design capacities, it is estimated that ten MSW incinerators account for 90% of the total design capacity for MSW incineration in country X.

The inventory preparer sends a request to the national statistics office, asking for the quantity of MSW generated in each state or province in 2004, the fraction disposed by incineration, and, if available, the waste composition and characteristics (these data are publicly available). According to the statistical data, a total of 5,000,000 tons of MSW were incinerated in country X during 2004. To complement this information and to estimate activity levels with a higher degree of confidence, questionnaires are sent to the ten largest MSW incinerators. According to the statistical data and/or information provided by the permitting authority, the developer of the inventory determines that these ten MSW incinerators are located in only two provinces or states in country X. Site visits are scheduled to confirm and collect information on technologies in use and gain intelligence on actual practices of the facilities.

The waste incineration plants are assigned to four classes according to their technologies, by using the data obtained through questionnaires and complemented by site visits. The corresponding 2005 Toolkit emission factors are selected for these four source classes, and release estimates are obtained by each of the activity rates with their respective emission factors. The results are presented in the table below.

Source group	Source category	Class		Activity rate (t/year)	Annual Release (g TEQ/a)					
					Air	Water	Land	Product	Residue	
									Fly ash	Bottom ash
1 Waste Incineration	1a MSW	1	Low technology combustion, no APCS	-						
		2	Controlled combustion with minimal APCS	2,000,000	700				1,000	30
		3	Controlled combustion with good APCS	2,000,000	60				400	14
		4	High technology combustion, sophisticated APCS	1,000,000	0.5				15	1.5

### **1b Hazardous waste incineration**

A request is sent to the national environmental permitting authority, asking for the number of HW incinerators with active permits in 2004, their basic designs, design capacities and locations. The permitting authority reports that 30 HW incinerators were permitted and active in country X during that year and provides the additional information requested for each incinerator.

A request is sent to the national statistics office, asking for the quantity of HW generated in each state or province in 2004 and the fraction disposed by incineration. According to the statistical data, a total of 200,000 tons of HW were incinerated in country X during 2004.

The HW incinerators are assigned to four classes according to their technologies. The corresponding 2005 Toolkit emission factors are selected for these four source classes, and release estimates are

obtained by each of the activity rates with their respective emission factors. The results are presented in the table below.

Source group	Source category	Class		Activity rate (t/year)	Annual Release (g TEQ/a)					
					Air	Water	Land	Product	Residue	
									Fly ash	Bottom ash
1 Waste Incineration	1b Hazardous Waste	1	Low technology combustion, no APCS	50,000	1'750				450	
		2	Controlled combustion with minimal APCS	100,000	35				90	
		3	Controlled combustion with good APCS	-						
		4	High technology combustion, sophisticated APCS	50,000	0.0375				1.5	

### 1c Medical waste incineration

In the case of medical waste incineration, the developer of the inventory obtains useful information from the Ministry of Health, including the total number of hospitalized patients in 2004. By visiting a typical incineration facility located at a typical hospital in country X, information on the type and quantities of medical waste incinerated is obtained and averaged per patient. The data collected through this approach and extrapolated to the country level is used to estimate the total activity rate for the reference year. Information on technologies in place in these typical facilities was also used to classify medical waste incineration sources and assign corresponding emission factors from the 2005 Toolkit 2005.

Source group	Source category	Class		Activity rate (t/year)	Annual Release (g TEQ/a)					
					Air	Water	Land	Product	Residue	
									Fly ash	Bottom ash
1 Waste Incineration	1c Medical Waste	3	Controlled, batch type combustion, good APCS	800,000	420				736	

### Updated inventory

Beginning in 2007, country X implements an action plan to reduce releases of unintentional POPs, as part of its National Implementation Plan. Measures are taken to reduce releases from waste incineration, in particular through phasing in BAT/BEP for waste incinerators, upgrading facilities and increasing recycling rates. In 2013, country X updates its inventory to assess the success of the measures

implemented. Data are collected for the reference year 2010, and the inventory is established according to the Toolkit methodology as revised in 2013.<sup>31</sup>

As a first step in the updating process, the examination of the baseline inventory is a crucial step. It shows to the new developer of the inventory where information can be found, and which information gaps need to be filled using extrapolation and expert judgment. The same approach is thus taken in the updated inventory as in the baseline, based on statistical data for 2010 that is obtained from the same sources used for the 2004 inventory.

The Toolkit edition from 2005, which was used for the baseline inventory was revised and the Toolkit 2013 is used by the developer to update the inventory. In order to maintain consistency over time, the developer has to examine if the emission factors have been changed. The emission factors for the source group waste incineration are the same in both Toolkit versions.

### **1a Municipal Solid Waste Incinerators**

According to the new data, the total amount of MSW incinerated in 2010 is 4,000,000 tons, a 20% decrease since 2004. This suggests that incentives to increase recycling rates in country X were successful in reducing the total amount of municipal waste sent to MSW incinerators. Through applying best available techniques for waste incinerators, all facilities have been significantly upgraded with improved technology since the development of the first inventory, and are assigned to the two classes with the lowest emission factors.

The results show, for instance, that further to the measures implemented under the action plan, releases to air from MSW incineration have dropped by 88% while total releases have fallen by 67%. This assessment was obtained through applying the same inventory approach and the same set of emission factors, therefore the results are readily comparable and the trends over time are consistent.

Source group	Source category	Class		Activity rate (t/year)	Annual Release (g TEQ/a)					
					Air	Water	Land	Product	Residue	
									Fly ash	Bottom ash
1 Waste Incineration	1a MSW	1	Low technology combustion, no APCS	-						
		2	Controlled combustion with minimal APCS	-						
		3	Controlled combustion with good APCS	3,000,000	90				600	21
		4	High technology combustion, sophisticated APCS	1,000,000	0.5				15	1.5

### **1b Hazardous waste incineration**

<sup>31</sup> NB: The dioxin emission factors for waste incineration were not revised/changed in the 2013 revised edition of the Toolkit. These are the same as in the Toolkit 2005.



The total annual destruction capacity for hazardous waste was estimated at 200,000 tons in 2010, remaining at constant levels since 2004. Facilities burning hazardous waste were equally upgraded through the introduction of best available techniques for incinerators:

Source group	Source category	Class	Activity rate (t/year)	Annual Release (g TEQ/a)						
				Air	Water	Land	Product	Residue		
								Fly ash	Bottom ash	
1 Waste Incineration	1b Hazardous Waste	1	Low technology combustion, no APCS	-						
		2	Controlled combustion with minimal APCS	-						
		3	Controlled combustion with good APCS	150,000	1.5				67.5	
		4	High technology combustion, sophisticated APCS	50,000	0.0375				1.5	

The results thus show a massive decrease in releases from this category (more than 99%), as a result of upgrading the old facilities burning hazardous waste. This conclusion is based on results obtained through the same approach and same set of emission factors as in the baseline inventory.

### 1c Medical waste incineration

Medical waste incineration rates were also unchanged in 2010, with all facilities classified as class 3 of the Toolkit. The data were obtained as in the baseline inventory, through extrapolation of typical facility-specific information based on the number of patients registered in the baseline year. Therefore releases from this category remained at constant levels since 2004.

Source group	Source category	Class	Activity rate (t/year)	Annual Release (g TEQ/a)						
				Air	Water	Land	Product	Residue		
								Fly ash	Bottom ash	
1 Waste Incineration	1c Medical Waste	3	Controlled, batch type combustion, good APCS	800,000	420				736	

### 1g Destruction of animal carcasses

In 2006, when the baseline inventory for 2004 was developed, no information was available to assess the rates of thermal destruction of animal carcasses in country X. This category was considered irrelevant for country X and excluded from the baseline inventory. In 2013, the developer of the inventory discovers that one old facility exists that is specialized in thermal destruction of carcasses. The activity rate for 2010 (the reference year in the updated inventory) is estimated at 1,000 t carcasses

destroyed. The emission factor applied is 50 µg TEQ/t, corresponding to old facilities with limited air pollution control. The overall emissions to air from this source category amount to 0.05 g TEQ/year:

$$\begin{aligned} \text{PCDD/PCDF released to air in 2010 (g TEQ/year)} &= \text{Quantity of carcasses} \times EF_{\text{Air}} \\ &= 1,000 \text{ t/yr} \times 50 \text{ } \mu\text{g TEQ/t} \\ &= \underline{0.05 \text{ g TEQ/year}} \end{aligned}$$

The immediate conclusion would be an increase in air emission from 0 to 0.05 g TEQ from 2004 to 2010. However, this particular source was equally present in country X in 2004 but not assessed in the baseline inventory because of lack of information. Consequently, the first inventory must be revised taking into account this new information. The results obtained for this source category in 2004 and 2010 can be compared only after the baseline release estimate has been revised.

### Revision of the baseline inventory

The revision of the baseline inventory is necessary to ensure consistency of trends in releases over time. In this example, only the estimates for one source category pertaining to the waste incineration group need to be revised.

#### 1g Destruction of animal carcasses

With the updating of the inventory in 2013, country X discovers new information about thermal destruction of animal carcasses which must be incorporated in the baseline inventory. This source was not accounted in the reference year 2004 due to lack of information. The developer of the inventory needs to assess retrospectively the activity rate of this source for the baseline year to enable the comparison of 2004 and 2010 release estimates.

The activity rates for the baseline year are re-estimated at 1'500 t, and revised release estimates calculated as below:

$$\begin{aligned} \text{PCDD/PCDF released to air in 2004 (g TEQ/year)} &= \text{Quantity of carcasses} \times EF_{\text{Air}} \\ &= 1'500 \text{ t/yr} \times 50 \text{ } \mu\text{g TEQ/t} \\ &= \underline{0.075 \text{ g TEQ/year}} \end{aligned}$$

The results show thus a decrease by 33% in releases to air from this category. If the new information was not incorporated to revise the baseline release estimate, the resulting trend would have been, on the contrary, an increase in releases from this source.

### Conclusion

This example shows that when updating the dioxin inventory, examination of the previous inventory is essential in order to identify quickly the approach used, find valuable information sources to estimate activity rates, use consistent expert judgment to fill information gaps, etc. It also shows that, besides changes in the Toolkit through its revision in 2013, new information that becomes available at the country level is equally important in triggering revision of baseline estimates of releases. If this revision is not performed, the results obtained for the different reference years cannot be compared and trends over time cannot be calculated.

## **Example Inventory 3 Source Group 2 Ferrous and Non-Ferrous Metal Production**

### **Introduction**

The purpose of this case study is to illustrate the process of inventory development, update and revision, focusing on, metal industry. This case study provides a hypothetical example for a Country X, including practical details on updating of the inventory to assess the evolution of emissions further to implementing strict measures as specified in the action plan developed as part of the NIP. The case study also includes essential information on the process of revision of the baseline inventory, which is triggered by revision of emission factors in the Toolkit and discovery of new information on sources which existed in the baseline but were not accounted for due to lack of proper information at that time, allowing to refine the baseline estimates and obtain comparable results.

### **Baseline inventory**

The baseline inventory of country X was conducted in 2006 using data collected for the 2004 reference year, according to the 2005 Toolkit methodology.

Using the following information sources, a list of relevant activity types and facility names was produced:

1. Listings of industrial activities in the Associations representing the sector,
2. Customs databases for imports of inputs for the foundry industry,
3. Industrial activities listed in trade guides for product offers,
4. Local authorities (Districts, Municipalities) and national government (Ministry for Environment).

Based on the questionnaire for Group 2 – Ferrous and Non-Ferrous Metal Production (Annex 3 of the Toolkit), an adapted questionnaire was developed and sent by e-mail or via fax in 2006, to the list of industries obtained. The heads of each company were requested to complete the necessary information and the activity data for reference year 2004.

Of the twelve categories of sources in this group, only four are relevant to the country in the 2004 baseline year, and are detailed below:

- 2c Iron and steel production and foundries,
- 2d Copper production,
- 2e Aluminum production,
- 2l Thermal wire reclamation.

In 2006 no information was available on activity levels and technologies for the metals smelting sector. To overcome this, the questionnaire was sent to all industries identified, a total of 11. All of them are engaged in secondary smelting of different materials with different qualities, as Country X has not developed primary production of metals from ores.

Of all industries, a sample of 5 was selected to be visited in order to verify the correct interpretation of the information requested in the questionnaire and the degree of accuracy of the information submitted by the responsible of the company.

The facilities visited were those with activities considered as more sensitive in the estimates of PCDD/PCDF emissions, either by the level of activity or the production and control technologies used. The companies selected covered between 80 and 85% of total ferrous and non ferrous production, so this helped to improve the confidence of the emissions estimates in this sector.

Open burning of stolen cables from power and telephone lines is an informal activity which frequently takes place in the country. The allowed recovery technology is the peeling of wire for subsequent entry into smelting furnaces, without PVC or other plastic materials. The informal activity is performed in poor conditions. The stolen wire amount in 2004 was obtained from the electricity transmission companies and from the telephone companies.

### 2c Iron and Steel Production and Foundries

In this subcategory a total of five facilities were identified, among which two produce a total of 120,000 tons of liquid steel a year, and three were iron foundries with a production of 30,000 tons per year. They were ordered into four classes taking into account the technologies used.

Source category	Class	Production (t/a)	Annual release (g TEQ/a)					Sub- Total (g TEQ/a)	
			Air	Water	Land	Product	Residue		
Iron and steel plants	1	Dirty scrap, scrap preheating, limited controls	20,000	0.200				0.300	0.50
	2	Clean scrap/virgin iron, afterburner, fabric filter	-						
	3	Clean scrap/virgin iron, BOF furnaces	-						
	4	Blast furnaces with APC	100,000	0.001					0.00
<i>Sub- Total</i>		<i>120,000</i>	<i>0.20</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0.300</i>	<i>0.50</i>	
Foundries	1	Cold air cupola or rotary drum, no APCS	10,000	0.100					0.10
	2	Rotary drum - fabric filter	20,000	0.086				0.004	0.09
	3	Cold air cupola, fabric filter	-						
	4	Hot air cupola or induction furnace, fabric filter	-						
<i>Sub- Total</i>		<i>30,000</i>	<i>0.186</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0.00</i>	<i>0.19</i>	
<b>Total</b>	<b>Iron and steel production plants and foundries</b>	<b>150,000</b>	<b>0.388</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0.304</b>	<b>0.69</b>	

### 2d Copper Production

A total of three companies were identified as active in secondary smelting of copper, with a total production of 68,000 tons per year. Among these, 60,000 tons are produced in modern, well-operated

plants, with a rapid quench system, bag filters and filter activated carbon. In this way, emissions are captured in the gas treatment system, while waste generated through the process is better controlled. The remaining 8,000 tons are produced in two basic technology plants without controls.

Class		Production (t/a)	Annual release (g TEQ/a)					Sub- Total (g TEQ/a)
			Air	Water	Land	Product	Residue	
1	Sec. Cu - Basic technology	8,000	6.400				5.040	11.44
2	Sec. Cu - Well controlled	-						
3	Sec. Cu - Optimized for PCDD/PCDF control	60,000	0.300				18.000	18.30
4	Smelting and casting of Cu/Cu alloys	-						
5	Prim. Cu, well-controlled, with some secondary feed materials	-						
6	Pure prim. Cu smelters with no secondary feed	-						
<b>Total</b>	<b>Copper production</b>	<b>68,000</b>	<b>6.700</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>23.0</b>	<b>29.8</b>

## 2e Aluminum Production

This sector involved a total of three plants for secondary aluminum production using scrap of varying quality. The emissions for the two classes are presented in the following table. It is worth mentioning that in the present case these values are rather low, without significant variations between the different classes.

Class		Production (t/a)	Annual release (g TEQ/a)					Sub- Total (g TEQ/a)
			Air	Water	Land	Product	Residue	
1	Processing scrap Al, minimal treatment of inputs, simple dust removal	5,000	0.750				1.000	1.75
2	Scrap treatment, well controlled, good APCS	-						
3	Scrap treatment, well-controlled, fabric filter, lime injection	15,000	0.075				1.500	1.58
4	Optimized proces for PCDD/PPCDF abatement	-						
5	Shavings/turnings drying (simple plants)	-						
6	Thermal de-oiling, rotary furnaces, afterburners, fabric filters	-						
7	Pure primary Al plants	-						
<b>Total</b>	<b>Aluminum production</b>	<b>20,000</b>	<b>0.825</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>2.5</b>	<b>3.3</b>

## 2l Thermal Wire Reclamation and e-waste recycling

To estimate emissions from wire burning, it was assumed that all stolen cables were burned in the open, so the country's copper smelters only receive bare wires. This will lead to an overestimation of the emissions which is however found acceptable due to lack of other information.

It is estimated that a total of 600 tons of cables were burned in the open in 2004. This is based on the length of stolen wire and weight per kilometer (kg/km), as provided by electricity transmission companies and phone companies. It was also assumed that the activities of electronic scrap recovery take place nationwide.

Class		Production (t/a)	Annual release (g TEQ/a)					Sub- Total (g TEQ/a)
			Air	Water	Land	Product	Residue	
1	Open burning of cable	600	3.000					3.00
2	Basic furnace with after burner, wet scrubber	-						
3	Burning electric motors, brake shoes, etc., afterburner	-						
<b>Total</b>	<b>Thermal wire reclamation</b>	<b>600</b>	<b>3.000</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>3.0</b>

### Update of the inventory

As part of the National Implementation Plan, the Country X has implemented a set of measures to reduce the generation and release of unintentional POPs. The baseline inventory was updated in 2013 to assess whether the implementation of such measures was successful. The Toolkit as revised in 2013 was used as a basis for updating release estimates. The update served to assess both the changes in volumes and types of activity taking place in the country, as well as the effectiveness of measures implemented to reduce levels of emissions.

The measures implemented to reduce the PCDD/PCDF emissions from other source categories, in particular waste management, and the rising value of metals on the market, has led to an increase in waste recycling and increasing rates of metal scrap recovery, mainly ferrous.

In addition, during the baseline survey performed in 2006 to produce the baseline inventory, several gaps in information were detected. Therefore the Government decided to require registration of smelting activities through the Ministry of Environment. Through this government decision, companies are obliged to update their information every four years. Due to this initiative, necessary information was readily available for processing, and the time needed to update the inventory was significantly reduced. This also allowed to identify the leading smelting activity in Country X, which had not been detected in the first inventory.

### 2c Iron and Steel Production and Foundries

In 2010, the same five industries remain, with an increase of 33% in production, which are still insignificant compared to the total releases form Group 2.

Source	Class	Production	Annual release (g TEQ/a)					Sub- Total
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Category			(t/a)	Air	Water	Land	Product	Residue	(g TEQ/a)
Iron and steel plants	1	Dirty scrap, scrap preheating, limited controls	25,000	0.250				0.375	0.625
	2	Clean scrap/virgin iron or dirty scrap, afterburner, fabric filter	-						
	3	Clean scrap/virgin iron or dirty scrap, EAF equipped with APCS, BOF furnaces	-						
	4	Blast furnaces with APCS	130,000	0.001					0.001
<i>Sub-Total</i>			<i>155,000</i>	<i>0.251</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0.375</i>	<i>0.626</i>
Foundries	1	Cold air cupola or hot air cupola or rotary drum, no APCS	5,000	0.050					0.050
	2	Rotary drum - fabric filter or wet scrubber	40,000	0.172				0.008	0.180
	3	Cold air cupola, fabric filter or wet scrubber	-						
	4	Hot air cupola or induction furnace, fabric filter or wet scrubber	-						
<i>Sub-Total</i>			<i>45,000</i>	<i>0.222</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0.0</i>	<i>0.230</i>
<b>Total</b>		<b>Iron and steel production plants and foundries</b>	<b>200,000</b>	<b>0.47</b>	<b>0.00</b>	<b>0.00</b>	<b>0.00</b>	<b>0.38</b>	<b>0.86</b>

For the year 2012, a new steel facility will be installed which will process 160 ton/day. This will be a Class 3 electric arc furnace plant equipped with air pollution control systems designed for lower PCDD/PCDF emissions. The government is also interested in projections of future releases to know how these will impact in the overall PCDD/PCDF emissions. The Toolkit 2013 methodology was thus used to forecast the new emissions showing an increase of +0.058 g TEQ/a in waste and in air emissions. This represents a net increase of 13.5% in this sub-category when compared to the 2010 scenario.

## 2d Copper Production

Further to the baseline survey conducted in Country X, according to which copper production accounted for 83% of the total PCDD/PCDF emissions from source group 2, the authorities implemented a plan to improve emission control in the copper foundry sector focusing on two aspects: adequate waste disposal to mitigate the impact on the environment, and upgrading of the two plants producing 8,000 t/a with basic technology. As a result, 6,000 tons are now produced with good air pollution control, and were moved from Class 1 to Class 2.

Class	Production (t/a)	Annual release (g TEQ/a)					Sub- Total (g TEQ/a)
		Air	Water	Land	Product	Residue	

1	Sec. Cu - Basic technology	2,000	1.600				1.260	2.860
2	Sec. Cu - Well controlled	6,000	0.300				3.780	4.080
3	Sec. Cu - Optimized for PCDD/PCDF control	60,000	0.300				18.000	18.300
4	Smelting and casting of Cu/Cu alloys	-						
5	Prim. Cu, well-controlled, with some secondary feed materials	-						
6	Pure prim. Cu smelters with no secondary feed	-						
<b>Total</b>	<b>Copper production</b>	<b>68,000</b>	<b>2.200</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>23.0</b>	<b>25.2</b>

## 2e Aluminum Production

In 2010, for the plants operated in Class 3 two aspects can be highlighted:

- the secondary aluminum production increased by 33% and
- 50% of solid residues were recycled internally, so waste emissions should be divided by two.

Class	Production (t/a)	Annual release (g TEQ/a)					Sub- Total (g TEQ/a)	
		Air	Water	Land	Product	Residue		
1	Processing scrap Al, minimal treatment of inputs, simple dust removal	5,000	0.750				1.000	1.750
2	Scrap treatment, well-controlled, fabric filter, lime injection	20,000	0.100				8.000/2 = 4.000	4.100
3	Optimized proces for PCDD/PPCDF abatement	-						
4	Shavings/turnings drying (simple plants)	-						
5	Thermal de-oiling, rotary furnaces, afterburners, fabric filters	-						
6	Primary Al plants	-						
<b>Total</b>	<b>Aluminum production</b>	<b>25,000</b>	<b>0.850</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>5.0</b>	<b>5.9</b>

## 2f Lead Production

The information available for the 2010 reference year shows that lead battery components free of PVC are used for smelting in rotary kiln with fabric filter, corresponding to Class 2.

Class	Production (t/a)	Annual release (g TEQ/a)					Sub- Total (g TEQ/a)
		Air	Water	Land	Product	Residue	



1	Sec. lead from scrap, PVC battery separators	-						
2	Sec. from PVC/Cl2 free scrap, some APCS	10,000	0.080				0.050	0.130
3	Sec. Lead, PVC/Cl2 free scrap in modern furnaces, with scrubber	-						
4	Pure primary lead production	-						
<b>Total</b>	<b>Lead production</b>	<b>10,000</b>	<b>0.080</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0.05</b>	<b>0.13</b>

## 2I Thermal Wire Reclamation and e-waste recycling

In 2010, it is estimated that 400 tons of wire have been burned in the open. This is less than for the baseline year (2004), due to changes in above-ground wires to underground wires, which decreases the possibility of theft.

Class	Production (t/a)	Annual release (g TEQ/a)					Sub- Total (g TEQ/a)
		Air	Water	Land	Product	Residue	
1	Open burning of cable	400	4.800				4.800
2	Open burning of circuit boards						
3	Basic furnace with after burner, wet scrubber						
4	Burning electric motors, brake shoes, etc., afterburner						
<b>Total</b>	<b>Thermal wire reclamation and e-waste recycling</b>	<b>400</b>	<b>4.800</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>4.8</b>

## Revision of the baseline inventory

In order to be able to compare the 2010 updated release estimates with the baseline inventory for 2004 to mark the progress in reducing PCDD/PCDF, the following aspects must be taken into account:

- 1) Classification of sources and emissions factors may vary due to revisions of the Toolkit.
- 2) Further activities were identified in 2010, for which data were not available in 2006.

The emission for 2004 need to be recalculated using the 2013 Toolkit to enable comparison.

The following table summarizes PCDD/PCDF emissions for a quick comparison between the 2004 and 2010 inventories.

Cat.	Class	Source categories	2004 recalculated				2010			
			Production (t/a)	Annual release (g TEQ/a)			Production (t/a)	Annual release (g TEQ/a)		
				Air	Residue	Total		Air	Residue	Total
<b>c</b>		<b>Iron and steel production plants and foundries</b>	<b>150,000</b>	<b>0.387</b>	<b>0.304</b>	<b>0.69</b>	<b>200,000</b>	<b>0.473</b>	<b>0.383</b>	<b>0.86</b>

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		<i>Iron and steel plants</i>	<i>120,000</i>	<i>0.201</i>	<i>0.3</i>	<i>0.50</i>	<i>155,000</i>	<i>0.251</i>	<i>0.375</i>	<i>0.63</i>
	1	Dirty scrap, scrap preheating, limited controls	20,000	0.2	0.3	0.50	25,000	0.25	0.375	0.63
	4	Blast furnaces with APCS	100,000	0.001	-	0.001	130,000	0.0013	-	0.001
		<i>Foundries</i>	<i>30,000</i>	<i>0.186</i>	<i>0.004</i>	<i>0.19</i>	<i>45,000</i>	<i>0.222</i>	<i>0.008</i>	<i>0.23</i>
	1	Cold air cupola or hot air cupola or rotary drum, no APCS	10,000	0.1	-	0.10	5,000	0.05		0.05
	2	Rotary drum - fabric filter or wet scrubber	20,000	0.086	0.004	0.09	40,000	0.172	0.008	0.18
<b>d</b>		<b>Copper production</b>	<b>68,000</b>	<b>6.7</b>	<b>23.04</b>	<b>29.7</b>	<b>68,000</b>	<b>2.2</b>	<b>23.04</b>	<b>25.2</b>
	1	Sec. Cu - Basic technology	8,000	6.4	5.04	11.4	2,000	1.6	1.26	2.9
	2	Sec. Cu - Well controlled	-	-	-	-	6,000	0.3	3.78	4.1
	3	Sec. Cu - Optimized for PCDD/PCDF control	60,000	0.3	18	18.3	60,000	0.3	18	18.3
<b>e</b>		<b>Aluminum production</b>	<b>20,000</b>	<b>0.825</b>	<b>7</b>	<b>7.8</b>	<b>25,000</b>	<b>0.85</b>	<b>5</b>	<b>5.9</b>
	1	Processing scrap Al, minimal treatment of inputs, simple dust removal	5,000	0.75	1	1.75	5,000	0.75	1	1.75
	2	Scrap treatment, well-controlled, fabric filter, lime injection	15,000	0.075	6	6.08	20,000	0.1	4	4.10
<b>f</b>		<b>Lead production</b>	<b>10,000</b>	<b>0.08</b>	<b>0.05</b>	<b>0.13</b>	<b>10,000</b>	<b>0.08</b>	<b>0.05</b>	<b>0.13</b>
	2	Sec. from PVC/Cl2 free scrap, some APCS	10,000	0.08	0.05	0.13	10,000	0.08	0.05	0.13
<b>l</b>		<b>Thermal wire reclamation and e-waste recycling</b>	<b>600</b>	<b>7.2</b>	<b>0</b>	<b>7.20</b>	<b>400</b>	<b>4.8</b>	<b>0</b>	<b>4.80</b>
	1	Open burning of cable	600	7.2		7.20	400	4.8		4.80
		<b>Ferrous and Non-Ferrous Metal Production</b>	<b>647,200</b>	<b>15.2</b>	<b>30.4</b>	<b>45.6</b>	<b>806,800</b>	<b>8.4</b>	<b>28.5</b>	<b>36.9</b>

It is observed that although a 25% increase has been registered in the production of metals from 2004 to 2010, total emissions from this source group have decreased by 19% overall. The total air emissions from metal production have been mostly impacted, with a total decrease of 45%.

The following sections show the revised calculations of the baseline inventory for each category.

## 2c Iron and Steel Production and Foundries

For this category is not necessary to recalculate the baseline releases, as the difference between the estimated emissions for both inventories is only due to increased production levels. In this category a

33% increase in production is registered. As this increase is based on adoption of improved technologies, there is not a consequent appreciable increase in emissions.

## 2d Copper Production

For this category is not necessary to recalculate the baseline releases. The decrease of 4.5 g TEQ/a in air emissions from 2004 to 2010 (15%) is also due improved technology in 2010.

## 2e Aluminum Production

For this category, it is necessary to recalculate the baseline releases due to the revision of the waste emission factor (for class 3, this changed from 100 to 400 µg TEQ/t).

Class	Production (t/a)	Annual release (g TEQ/a)					Sub- Total (g TEQ/a)	
		Air	Water	Land	Product	Residue		
1	Processing scrap Al, minimal treatment of inputs, simple dust removal	5,000	0.750				1.000	1.750
3	Scrap treatment, well-controlled, fabric filter, lime injection	15,000	0.075				6.000	6.075
4	Optimized process for PCDD/PPCDF abatement	-						
5	Shavings/turnings drying (simple plants)	-						
6	Thermal de-oiling, rotary furnaces, afterburners, fabric filters	-						
7	Primary Al plants	-						
<b>Total</b>	<b>Aluminum production</b>	<b>20.000</b>	<b>0.825</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>7.0</b>	<b>7.8</b>

Thus, in this category, a 33% increase in production produced an increase of 2 g TEQ/a in waste, which represents an increase of 26% compared to 2004 emissions in the secondary aluminum production.

## 2f Lead Production

For the year 2004, lead from battery components was melted in country X. However, this activity was not considered in the baseline inventory as it was not detected due to limitations in the survey. This new information should be included in the revised baseline inventory.

From the information available, it is estimated that in 2004, the activity took place at the same facility as in 2010, and with the same level of production, resulting in the same emissions than those estimated in 2010.

## 2l Thermal Wire Reclamation and e-waste recycling

Despite lower amounts of wire burnt in the open in 2010, by comparing to 2004 and 2010 release levels, PCDD/PCDF emissions are shown to increase. This is because the air emission factor for open burning of

cable has been revised and is significantly higher in the Toolkit 2013 than in the 2005 edition. Therefore the baseline releases need to be recalculated using the revised emission factor.

Class	Production (t/a)	Annual release (g TEQ/a)					Sub- Total (g TEQ/a)	
		Air	Water	Land	Product	Residue		
1	Open burning of cable	600	7.200					7.200
2	Open burning of circuit boards	-						
3	Basic furnace with after burner, wet scrubber	-						
4	Burning electric motors, brake shoes, etc., afterburner	-						
<b>Total</b>	<b>Thermal wire reclamation and e-waste recycling</b>	<b>600</b>	<b>7.200</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>7.2</b>

Thus, the decrease in releases from this source category is directly proportional to the decrease in the amount of burned wires, *i.e.* by 33%.

## Conclusion

When updating the PCDD/PCDF inventory, it is necessary to review the baseline/previous inventories, due to a number of reasons:

- The Toolkit is regularly updated (emission sources and emission factors).
- The identification of additional sources in the updated inventory, for which information was not yet available at the time the previous inventories were conducted.
- The improvement of the estimates of activity rates in some complex categories, requiring a review of previous inventory estimates. This is not specifically addressed in this case study.

The process to update and, when necessary, revise the inventory is essential to guarantee the comparability among results and establishing trends over time. Data quality and confidence in inventory results can be improved by site visits using a limited number of significant facilities. It is worth to include those facilities which have the potential to contribute more to the inventory, *i.e.* large facilities contributing to a large part of the overall production of the sector.

Finally, the process of collecting information for the inventory updating helps to identify gaps and inconsistencies in available information. This offers the opportunity for a practical analysis and a chance to improve and implement better mechanisms for collecting reliable information that may decrease the time needed in future updates and improve the quality of past estimates through revision of previous inventories to fill such gaps.

## **Example Inventory 4 Source Group 3 Power Generation and Heating**

### **Introduction**

The purpose of this case study is to illustrate the process of inventory development, update and revision, focusing on a single source group: Power generation and heating. We will consider a hypothetical example of a PCDD/PCDF inventory in country X, and describe the baseline inventory process, its update and revision for this particular source group.

### **Baseline inventory**

The total share of fuels in indigenous energy production in country X can be broken down as follows: 55% from hard coal, 37% from brown coal and the remaining 8% comes from gas, oil and hydro. Hard coal is thus the basic fossil fuel burned in households not only for heating, but also for cooking.

National activity statistics for the baseline reference year (2001) provide the following consumption figures:

- hard coal 174,338 TJ
- lignite 980 TJ
- high methane natural gas 110,658 TJ
- nitrified natural gas 16,953 TJ
- LPG 20,812 TJ
- light fuel oil 17,496 TJ

By grouping the fuels according to type (solid, liquid, gaseous) we obtain the following figures:

- coal 175,318 TJ
- oil 17,496 TJ
- natural gas 148,423 TJ

### **3e Household Heating and Cooking with Fossil Fuels**

One of the main sources of PCDD/PCDF releases in country X comes from combustion processes in household boilers and furnaces, where commercial fuels are frequently co-combusted with household waste. The municipal and housing sector has a dominant share in PCDD/PCDF emissions, as the main fuel used in this sector is hard coal, with an annual consumption of 9 million tons.

The 2003 Toolkit applies an emission factor for burning of coal in residential heating systems of 70 µg I-TEQ/TJ corresponding to approximately 2 µg I-TEQ/t. The default emission factor was derived from mean values reported between 1.6 and 50 µg I-TEQ/t of coal burned. Several recent measurements indicate that the emission from the residential burning of coal in country X may be much higher.

These results indicate that the emission factor for residential burning of coal - even though the coal is not co-combusted with waste - may be significantly higher than the default emission factor of the

Standardized Toolkit. The default emission factor is still used as a medium estimate, but it is estimated that the real average emission factor is likely to be higher rather than lower, and a range of 35-1,000 µg I-TEQ/t will be applied.

The resulting annual releases to air are presented in the table below:

Source category	Source Class	Activity rate TJ/year	EF <sub>Air</sub> µg I-TEQ/t		Annual release to air (g TEQ/a)	
			Medium (Toolkit 2003)	Range	Medium	Range
Domestic heating and cooking – fossil fuels	Coal fired stoves	219,484	70	30-1,000	15	6.6-200

### Update of the inventory

In 2008, new emission factors are published in country X based on specific measurements of emissions from coal fired stoves. These country-specific factors are then used with higher confidence to update the inventory. Activity rates are comparable with those estimated for the baseline year, and are equally derived from national statistics, as in the baseline inventory.

Source category	Source Class	Activity rate TJ/year	EF <sub>Air</sub> µg I-TEQ/t Country-specific	Annual release to air (g TEQ/a)
Domestic heating and cooking – fossil fuels	Coal fired stoves	200,000	115	23

The results show a slight increase in releases, although activity rates were maintained at relatively constant levels. This is clearly due to applying a different set of emission factors, which were derived to better reflect the national circumstances in country X.

### Revision of the baseline inventory

The revision of the baseline inventory is thus necessary to ensure consistency of trends in releases over time. In this example, the revision is triggered by scientific findings and developments, allowing country X to re-calculate releases by using an own set of emission factors developed to better reflect national circumstances.

Source category	Source Class	Activity rate TJ/year	EF <sub>Air</sub> µg I-TEQ/t Country-specific	Annual release to air (g TEQ/a)
Domestic heating and cooking – fossil fuels	Coal fired stoves	219,484	115	25.24

The revised baseline estimates show that indeed a decrease in releases from this major source has happened from 2001 till 2008.

### **Conclusion**

This example shows that when applying own emission factors, through periodic refinement of the methodology to develop the PCDD/PCDF inventory, revisions of the previous inventories are equally needed. Besides changes in the Toolkit methodology through its revision in 2013, better information becoming available at the country level, including through direct measurements of emissions and development of more specific emission factors, is an equally important triggering factor to revise baseline estimates of releases. If the revision of the baseline is not performed, the results obtained for the different reference years are not readily comparable and trends over time cannot be estimated.

## Example Inventory 5 Source Group 4 Mineral Products

### Introduction

The purpose of this case study is to illustrate the process of inventory development, update and revision. We will consider a hypothetical example of an inventory of country X, and describe the inventory process focusing on the source group 4 Mineral Products.

### Baseline inventory

Let's consider a hypothetical inventory of country X. **The baseline inventory** is developed in 2006, based on data collected for the reference year 2005 and by using the Toolkit 2005 methodology. The baseline inventory estimated that approximately 15,000 tons of bricks were manufactured each year based from statistical data obtained from the manufacturing industry. The technologies used in the manufacturing industry have no dust control systems in place and do NOT use contaminated fuels. The total annual releases for the baseline year were calculated based on the Toolkit 2005 methodology, by applying an emission factor for air of 0.2 µg TEQ/t of brick manufactured. The baseline releases to air from brick manufacturing were thus estimated at 0.003 g TEQ/year.

$$\begin{aligned} \text{Baseline PCDD/PCDF released to air in 2005 (g TEQ/year)} &= \text{Quantity of bricks manufactured} \times EF_{\text{Air}} \\ &= 15,000 \text{ t/yr} \times 0.2 \text{ } \mu\text{g TEQ/t} = \underline{0.003 \text{ g TEQ/year}} \end{aligned}$$

### Update of the inventory

**The updated inventory** is developed in 2013, based on data collected for the reference year 2010 and the Toolkit methodology as revised in 2013. Activity rates for this source had been assessed at around 15,000 tons of bricks produced annually for the baseline year. The corresponding emission factor has been revised since the first inventory and is much lower than the one used for the baseline inventory:  $EF_{\text{Air}}$  is now 0.02 µg TEQ/t of brick produced using technologies that have no emission abatement technology in place and using non-contaminated fuels. This is in contrast to 0.2 µg TEQ/t that had previously been used for this technology. In addition in this category, there are new emission factors for Products (0.006 µg TEQ/t) and Residues (0.002 µg TEQ/t). The total annual release based on the Toolkit 2013 methodology is determined as below:

$$\begin{aligned} \text{PCDD/PCDF released to air in 2010 (g TEQ/year)} &= \text{Quantity of bricks manufactured} \times EF_{\text{Air}} \\ &= 15,000 \text{ t/yr} \times 0.02 \text{ } \mu\text{g TEQ/t} = \underline{0.0003 \text{ g TEQ/year}} \end{aligned}$$

This is approximated to 0g TEQ/year in the excel tables.

$$\begin{aligned} \text{PCDD/PCDF to products in 2010 (g TEQ/year)} &= \text{Quantity of bricks manufactured} \times EF_{\text{Product}} \\ &= 15,000 \text{ t/yr} \times 0.006 \text{ } \mu\text{g TEQ/t} = \underline{0.00009 \text{ g TEQ/year}} \end{aligned}$$

This is approximated to 0 g TEQ/year in the excel tables.

$$\begin{aligned} \text{PCDD/PCDF to residues in 2010 (g TEQ/year)} &= \text{Quantity of bricks manufactured} \times EF_{\text{Residue}} \\ &= 15,000 \text{ t/yr} \times 0.002 \text{ } \mu\text{g TEQ/t} = \underline{0.00003 \text{ g TEQ/year}} \end{aligned}$$

This is approximated to 0gTEQ/year in the excel tables.



**TOTAL RELEASES IN 2010 = sum of TEQs released to the different for the media = 0 g TEQ/year**

Thus based on the 2013 Toolkit methodology, the updated release levels for this category for the baseline year 2010, changes from 0.003gTEQ/yr to 0g TEQ/yr.

### Revised baseline inventory

Based on new statistical data available, it was now possible to estimate the total brick production in the country which will include bricks from commercial production and artisanal brick production as opposed to baseline year which only had data from the commercial manufacturing industries. This will give a better estimate of activity rate arising from this source category.

From statistical data 35,000 housing units are built per year and of these, approximately 16% are constructed using bricks. Assuming that each housing unit will use approximately 15,000 bricks and each weighing approximately 2.5kg, the resulting activity rate will be as follows:

#### Calculation of activity rate:

Total number of housing units built per year	=	35,000
Total number of units built using bricks is 16% of total	=	35,000 x 0.16
	=	5,600 units
Bricks used per unit appx 15,000 and assuming 10% waste	=	15,000 + (15,000 x 0.1)
	=	16,500 bricks
Total number of bricks used for 5600 units	=	16,500 x 5,600
	=	92,400,000 bricks
Total tons of bricks produced/yr assuming 2.5kg per brick	=	92,400,000 x 2.5/1000 tons
	=	231,000 tons

In determining the activity rates based on construction data, there is a level of uncertainty that is inherent because of use of a uniform size of house unit, assumed identical sizes for both commercial and artisanal bricks and also not taking into consideration other buildings that are not residential units but use bricks for construction .

Calculation of release estimates:

$$\begin{aligned} \text{Revised baseline PCDD/PCDF released to air (g TEQ/year)} &= \text{Quantity of bricks manufactured} \times EF_{Air} \\ &= 231,000 \text{ t/yr} \times 0.02 \mu\text{g TEQ/t} = 0.005 \text{ g TEQ/year} \end{aligned}$$

$$\begin{aligned} \text{Revised baseline PCDD/PCDF to products (g TEQ/year)} &= \text{Quantity of bricks manufactured} \times EF_{Product} \\ &= 231,000 \text{ t/yr} \times 0.006 \mu\text{g TEQ/t} = 0.001 \text{ g TEQ/year} \end{aligned}$$

$$\begin{aligned} \text{Revised baseline PCDD/PCDF to residues (g TEQ/year)} &= \text{Quantity of bricks manufactured} \times EF_{Residue} \\ &= 231,000 \text{ t/yr} \times 0.002 \mu\text{g TEQ/t} = 0.00046 \text{ g TEQ/year} \end{aligned}$$

This is approximated to 0g TEQ/yr in the excel tables.

***TOTAL RELEASES IN 2005 = 0.006 g TEQ/year***

Based on the revised emission factors in the 2013 Toolkit, and improved activity rate data, this is a better estimate of the releases from this category for the baseline year 2005.

**Conclusion**

Revising the release levels from this category is advised, since the revised emission factor values in the 2013 Toolkit may affect the release levels by one order of magnitude as compared with those that had been determined using the previous emission factors. It is important to establish activity rates in artisan brick production especially in situations where there are no statistics for production rates and there are indications that the estimated artisan production rates are significantly high as compared to commercial production. Construction/building statistics may assist in arriving at a reasonable estimate. It is also important to establish the types of fuels used, as the use of contaminated fuels influences the emission factor by one order of magnitude.

## **Example Inventory 6 Source Group 5 Transport**

### **Introduction**

The purpose of this case study is to illustrate the process of inventory development, update and revision, including the various triggering factors that may come into play in this process. We will consider a hypothetical example of an inventory of country X, and describe the baseline inventory process, its update and revision, focusing on source group 5 Transport.

### **Baseline inventory**

Country X prepares its first inventory of dioxins and furans in 2006 to support the development of the action plan as required by Article 5 of the Convention and included in the National Implementation Plan pursuant to Article 7. Activity data for the different sources of PCDD/PCDF in country X were collected for the reference year 2004 (baseline year). The inventory is developed by applying the Toolkit 2005 methodology and the emission factors specified in that version of the Toolkit.

All four source categories included in this source group are relevant for country X in the baseline year. These are presented below.

According to the Toolkit 2005 methodology, activity rates for transport should be expressed as volumes of fuel used by category of fuel and transport. During the process of activity data collection, information on actual amounts of fuel used in the transport sector annually (gasoline, ethanol, diesel fuel, kerosene, residual oil, jet fuel etc.) at the national level was found from the national statistics office. According to these data, in 2004 in country X, 1,000,000 tons of gasoline, 500,000 tons of diesel fuel, 100,000 tons of heavy fuel (residual) oil, 50,000 tons of kerosene, 10,000 tons of LPG and 5,000,000 m<sup>3</sup> of CNG were used for transportation. The data provides details on quantities of fuel according to fuel type and sector (road transport, railway transport, mobile machinery in agriculture, construction, forest industry etc.).

However, no data on distribution of leaded and unleaded gasoline are publicly available; no data on distribution of fuel consumption according to the type of vehicles (4-stroke and 2-stroke) and its ecological class (without catalyst and with catalyst) are available.

To complement this information and be able to obtain estimates of fuel distribution with a higher degree of confidence, questionnaires have been sent to the main offices and consumers of fuel in the country: Ministry of Transport, Ministry of Trade, Police Agency, Railroad agency, Aviation Company. The objectives of the questionnaires were to obtain more detailed data on the vehicle fleet.

It was thus established that data are available on request on the number of registered vehicles per type of vehicle. Data on the year of production of the registered cars were also obtained, but no account of vehicles by ecological characteristics (with or without catalysts) was available.

According to these data obtained by the developer of the inventory, 100,000 tons of leaded gasoline were imported in 2004, but the distribution between 4-stroke and 2-stroke vehicles could not be obtained. Questionnaires showed that 2-stroke vehicles are more often fueled with leaded gasoline in comparison with 4-stroke vehicles; expert judgment was used to estimate the distribution of leaded gasoline between 4-stroke and 2-stroke vehicles; this was assumed to be 80%:20%. For the distribution

of fuel per type of vehicle, proxies were estimated by using data on the number of registered cars according to the type and the specific fuel consumption per unit.

For the distribution of vehicles according to ecological characteristics, data on the age of vehicles were used. It was assumed that vehicles which comply with Euro 2 class and higher are equipped with catalyts. It was assumed that vehicles imported from the European Community comply with the highest Euro class which was in force at the time of the vehicle production. Further, questionnaires allowed to estimate the distribution of vehicles according to the year of production, and through this - between Euro classes.

The amount of gasoline consumed was then distributed between 4-stroke and 2-stroke engines according to number of vehicles in a category, and averaged specific consumption of fuel per vehicle type was of 95 and 5%.

All diesel fuel engines were assigned to category 5c – Diesel engines, including light and heavy duty vehicles, railway transport, construction, agricultural and other mobile machinery.

The corresponding 2005 Toolkit emission factors were applied to these four source classes, and release estimates obtained by multiplying the activity rates with the emission factors. The results are presented in the table below. No PCDD/PCDF emission factors were available for airplanes (kerosene, jet fuel etc.) and for vehicles fueled with LPG and CNG, therefore releases from these sources were not assessed.

The total PCDD/PCDF releases to air from the transport sector in 2004 were of 0.968 g TEQ. No emission to other media was accounted.

**Baseline inventory (reference year: 2004)**

5 - Transport		Activity rate t/year	Air EF (µg TEQ/t)	Annual Release (g TEQ/a)				
				Air	Water	Land	Product	Residue
Source categories								
a	4-Stroke engines	1000000						
	Leaded fuel	80000	2.2	0.176				
	Unleaded fuel without catalyst	720000	0.1	0.072				
	Unleaded fuel with catalyst	100000	0.00	0				
b	2-Stroke engines	100000		-				
	Leaded fuel	20000	3.5	0.07				
	Unleaded fuel without catalyst	80000	2.5	0.2				
c	Diesel engines	500000	0.1	0.05				
d	Heavy oil fired engines	100000	4	0.4				
TOTAL for the source group				0.968				

## Update of the inventory

Starting with 2007, country X implements an action plan to reduce releases of unintentional POPs, as part of its National Implementation Plan. Measures are taken to reduce releases from transport, in particular through phasing out leaded gasoline, upgrading of vehicle fleet (through implementation of stricter standards for vehicles, higher taxes for import of old cars, programs of old vehicle replacement etc.). In 2013, country X updates its inventory to assess the success of the measures implemented. Data are collected for the reference year 2010, and the inventory is established according to the Toolkit methodology as revised in 2013.

As a first step in the inventory updating process, the examination of the baseline inventory essential to show to the developer of the inventory where the information can be found, and which areas need extrapolation and expert judgment to fill gaps. The same approach is thus taken in the updated inventory as in the baseline, based on statistical data from the same sources, selective questionnaires sent to profile ministries, agencies and associations.

According to the new set of data, the total amount of fuel used for transport in 2010 was of 2'400'000 tons, registering a 50% increase since 2004. Leaded gasoline was phased out, and the share of fuel used for 2-stroke engines was reduced by 30%. A program on updating the car fleet was implemented; as a result, the share of 4-stroke vehicles with catalysts increased by 20%. Ethanol powered vehicles have replaced part of the gasoline powered vehicles; ethanol consumption is now estimated at 100'000 tons. This new information showed that 20% of vehicles still use inadequate catalyst or not at all, and were considered as not equipped with catalyst. Diesel fuel was partially replaced by biodiesel (35000 tons of biodiesel were used in 2010).

Available literature showed that ethanol powered vehicles have a lower emission factor than gasoline powered vehicles, and that biodiesel powered vehicles emit less PCDD/PCDF than diesel powered vehicles. Thus, the emission factor for ethanol vehicles equipped with catalyst is close to zero, and the emission factor for biodiesel<sup>20</sup> is 0.07 µg TEQ/t.

**Results of the updated emission inventory (reference year: 2010)** are shown below.

5 - Transport		Activity rate, t/year	EF (µg TEQ/t)	Annual Release (g TEQ/a)				
				Air	Water	Land	Product	Residue
a	4-Stroke engines	1500000						
	Leaded fuel	0	2.2	0				
	Unleaded fuel without catalyst or with inadequate catalyst	1080000	0.1	0.108				
	Unleaded fuel with catalyst	320000	0.001	0.00032				

	Ethanol with catalyst	100000	0.0007	0.00007				
b	2-Stroke engines	120000						
	Leaded fuel	0	3.5	0				
	Unleaded fuel without catalyst	120000	2.5	0.3				
c	Diesel engines	700000						
	Regular diesel	665000	0.1	0.067				
	Biodiesel (20% biofuel)	35000	0.07	0.002				
d	Heavy oil fired engines	100000	2	0.2				
Total for the source group				0.677				

The total dioxin and furan emissions were of 0.677 g TEQ in 2010.

### Revision of the baseline inventory

The revision of the baseline inventory is necessary to ensure the consistency in trends in releases over time. In this example, the estimates for two source category pertaining to the transport group need to be revised.

With the updating of the inventory in 2013, country X discovers new information on the consumption of leaded gasoline by 4- and 2-stroke engines, which needs to be incorporated in the baseline inventory. The developer of the inventory needs to retrospectively assess the activity rate for this source and for the baseline year to enable the comparison of 2004 and 2010 release estimates. The volume of leaded fuel burned in 4- and 2-stroke engines in 2004 was thus reassessed.

The activity rates for leaded fuel the baseline year are re-estimated at 150000 t for 4-stroke and 50000 t for 2-stroke vehicles, and introducing the revised emission factors for gasoline and ethanol vehicles with catalyst and for heavy oil, the revised baseline release estimates are shown in the table below:

### Revised baseline inventory (reference year: 2004)

5 - Transport		Activity rate (t/year)	EF (µg TEQ/t)	Annual Release (g TEQ/a)				
				Air	Water	Land	Product	Residue
	<b>Source categories</b>							
a	4-Stroke engines	1,000,000						
	Leaded fuel	150,000	2.2	0.33				
	Unleaded fuel without catalyst or with inadequate catalyst	720,000	0.1	0.072				

	Unleaded fuel with catalyst	100,000	0.001	0.0001				
b	2-Stroke engines	100,000						
	Leaded fuel*	50,000	3.5	0.175				
	Unleaded fuel without catalyst	80,000	2.5	0.2				
c	Diesel engines	500,000	0.1	0.05				
d	Heavy oil fired engines	100,000	2	0.2				
Total for the source group				1.027				

The corresponding total dioxin and furan emission revised for the 2004 baseline year was of 1.027 g TEQ.

The results show a decrease of 34% in total releases from group 5 - Transport. If the new information was not incorporated to revise the baseline release estimate, the resulting trend would not have been the same, with an emission reduction of only 9%. The results of the inventory show that despite of the increase in motor fuel consumption in a country X, incentives to phase out leaded gasoline, switching to ethanol and upgrading of the vehicle fleet were important measures to reduce the overall PCDD/PCDF emissions from the transport sector.

This assessment was obtained through applying the same inventory approach and the same set of emission factors, therefore the results are readily comparable and the trends over time are consistent.

## Example inventory 7 Source Group 6 Open Burning Processes

### Introduction

The hypothetical inventory example presented below aims to illustrate the process of inventory development, update and revision for source group 6: Open Burning Processes. It takes into consideration some of the triggering factors for updating and revision that are specific to this particular source group.

### Baseline Inventory

In country X, open burning processes releasing PCDD/PCDF mainly include biomass burning to clean the fields and domestic waste burning. The baseline inventory of country X is developed in 2006 based on data collected for the reference year 2004. The developer of the inventory found only limited data on activity levels for this sector. Data on forest fires was collected for instance from the Ministry of Agriculture and Forestry. Nevertheless, expert judgment was an essential tool to calculate releases from open burning.

#### 6a Biomass burning

According to the statistics provided by the Ministry of Agriculture and Forestry of country X, three major fire incidents have occurred in 2004, affecting a total of 20'000 hectares of forest. Data from a national forest inventory and analysis program and a number of studies estimating forest biomass in country X using remote sensing and satellite products show that forest biomass density across the country is on average 150 tons/ha. The baseline activity rate for this source class is thus estimated at 3'000'000 tons burnt annually.

Secondly, the extent of crop residue burning is very difficult to estimate. The actual amount varies dramatically from year to year, depending upon amounts of rainfall, cropping patterns and weather conditions during and after the harvest season. Some years, burning may take place over quite a long fall season, or even be delayed to the following spring. As such, it is very difficult to estimate the extent of burning in a given year, or to analyze trends.

Assumptions are thus needed to quantify the quantity of agricultural residues that are burnt annually. Two assumptions are made by the developer of the inventory, according to a similar study:

- 1) that the amount of agricultural residue able to be burned was equal to the total crop production, and
- 2) that 80% of residues were burned in the developing world and 50% of residues were burned in the developed world for any given year.

Based on these assumptions, activity rates for agricultural residue burning were estimated at 500'000 tons of material burnt in 2004. Dioxin and furan releases from these sources were calculated according to the Toolkit (2005) methodology and the corresponding results are presented below.

Source category	Source Class	Activity rate (t/year)	Annual release (g TEQ/a)					Total
			Air	Water	Land	Product	Residue	
Biomass	Forest fires	3'000'000	15		12			27



burning								
	Agricultural residue burning, poor combustion conditions	500,000	15		5			20

### 6b Waste burning and accidental fires

The only relevant source contributing to dioxin and furan releases from this category is domestic waste burning. Data on domestic waste burning are not readily available in country X. The developer of the inventory therefore needs to estimate activity rates for this sector based on assumptions and expert judgment. The average amount of waste produced in urban areas is of 0.7 kg per capita per day and of 0.5 kg per capita per day in rural areas. From the total amount of waste generated in urban areas, 70% are collected for reuse, incineration or disposal, leaving 30% that can be burned in backyard fires. From the total amount of waste generated in rural areas, it is considered that 20% are burnt in the open, since a greater fraction is used for composting.

The estimated amount of domestic waste burnt annually is of 60,000 tons in 2004. The total annual releases are calculated by multiplying this activity rate with the corresponding emission factor. The results are shown in the table below:

Source category	Source Class	Activity rate (t/year)	Annual release (g TEQ/a)					Total
			Air	Water	Land	Product	Residue	
Waste burning and accidental fires	Open burning of domestic waste	60,000	18		36			54

### Update of the inventory

Country X implements measures to reduce releases from open burning as part of the action plan within its National Implementation Plan. The measures are based on providing incentives to avoid open burning and manage waste in a more appropriate manner: through education and awareness raising programmes, better infrastructure and enforcement. In 2013, country X initiates an update of the inventory to assess the success of these measures. The activity data used for updating release estimates are collected for the reference year 2010, while the inventory is developed according to the Toolkit methodology as revised in 2013.

### 6a Biomass burning

The 2010 activity data are estimated according to the same approach and using the same expert judgment and assumptions as in the baseline inventory. Only two fire incidents were registered in 2010, totaling 2'000'000 tons of forest material burnt annually.

Furthermore, in addition to agricultural residue burning, a new class of major relevance for country X is included in the inventory – sugarcane burning. This class is newly added in the 2013 version of the Toolkit, and new emission factors were developed and are now available for this very specific source. Agricultural residues and sugarcane residues burnt in 2010 are estimated according to the same assumptions as in the baseline inventory and amount to 300'000 tons and 100'000 tons material burnt respectively. The resulting release estimates are shown below:

Source category	Source Class	Activity rate (t/year)	Annual release (g TEQ/a)					Total
			Air	Water	Land	Product	Residue	
Biomass burning	Agricultural residue burning, poor combustion conditions	300,000	9		3			11
	Sugarcane burning	100'000	0.4		0.005			0.45
	Forest fires	2'000'000	2		0.3			2.3

The immediate conclusion after the updating of the inventory would be a drastic reduction in emissions to air from agricultural residue burning (-40%) and forest fires (-87%) and an increase from 0 to 2 g TEQ in emissions to air from sugarcane burning. This conclusion would not take into account the fact that the emission factors have equally been revised and are much lower in the 2013 edition of the Toolkit than in the 2005 edition. This has an impact on the resulting estimates of releases, contributing to lower emission values. In addition, the new class of sugarcane burning for which emission factors were not available in the 2005 edition of the Toolkit, will also have to be assessed separately in the baseline inventory, so that the same basis for calculation (and same emission factors) and the same scheme of classification of sources be used for both reference years.

### **6b Waste burning and accidental fires**

2010 activity rates for open burning of domestic waste are calculated by extrapolating per capita waste production to population levels in urban and rural areas, and using the same assumptions concerning the fraction of waste that is burnt in the open in these areas. Approximately 70,000 tons of domestic waste are considered to be burnt annually. The total annual releases in 2010 are calculated as below, based on the Toolkit 2013 methodology:

Source category	Source Class	Activity rate (t/year)	Annual release (g TEQ/a)					Total
			Air	Water	Land	Product	Residue	
Waste burning and accidental fires	Open burning of domestic waste	70,000	2.8		0.07			2.9

Despite the increase in the quantity of domestic waste burnt in the open, releases are shown to be much lower than in the baseline year (-85%). This is due to the revision of the respective emission factor *e.g.*, for air, the emission factor was revised from 300 µg TEQ/t to 40 µg TEQ/t. To be able to assess the actual trend in releases over time, a revision of the baseline inventory is thus necessary use the same basis for calculation for both 2004 and 2010 estimates.

### Revision of the baseline inventory

Two triggering factors come into play in this case prompting the need for revision: one is the revision of emission factors in the Toolkit, and the second one is the addition of new source classes to the Toolkit classification. To be able to compare release estimates in 2004 and 2010, the same methodology, the same basis for calculation (the same emission factors) need to be consistently used in the different inventories, along with the same source classification scheme.

There is a need to go back to the baseline release estimates for this source group and re-calculate those estimates according to the same methodology and approach as used in the updated inventory. The revised baseline estimate will be the product of the baseline activity levels and the revised emission factors taken from the Toolkit 2013 methodology.

#### 6a Biomass burning

The baseline release estimates are re-calculated by applying the 2013 set of Toolkit emission factors and the classification of sources put forward in the 2013 version of the Toolkit. From the 400'000 tons of agricultural residues were considered to be burnt in the open in 2004 (the baseline year), 100'000 tons were actually sugarcane residues. As at the time the baseline inventory was developed there were no emission factors available for sugarcane burning, those residues were assessed together with the other agricultural crops. The releases are re-calculated by including this additional class and applying the emission factors proposed in the Toolkit 2013 methodology:

Source category	Source Class	Activity rate (t/year)	Annual release (g TEQ/a)					Total
			Air	Water	Land	Product	Residue	
Biomass burning	Agricultural residue burning, poor combustion conditions	300,000	9		3			11
	Sugarcane burning	100'000	0.4		0.005			0.4
	Forest fires	3'000'000	3		0.45			3.45

The comparison between the updated and revised inventory accurately shows that the releases from agricultural residue burning and sugarcane burning are at a constant level since 2004. Only the forest fire emissions are down by one third, corresponding to an equivalent decrease in activity rates.

#### 6a Waste burning and accidental fires

The re-calculation of release estimates from this source category is simply done by multiplying the baseline activity levels with the revised emission factors taken from the 2013 methodology. As no new or corrected information has become available that would influence activity level estimates, these are the same as in the 2004 inventory: 60'000 tons of domestic waste burnt annually. The revised baseline release estimates are shown in the table below:

Source category	Source Class	Activity rate (t/year)	Annual release (g TEQ/a)					Total
			Air	Water	Land	Product	Residue	
Waste burning and accidental fires	Open burning of domestic waste	60,000	2.4		0.06			2.5

The results demonstrate that between 2004 and 2010 there was an actual increase in emissions from 2.5 to 2.9 g TEQ/year. If the baseline estimate was revised by using the same emission factors for the calculation, the conclusion of a reduction in releases from 2004 to 2010 would have been largely amiss.

### Conclusion

The Toolkit emission factors for open burning were significantly revised since the 2005 edition, and new source classes added to the respective categories. These two factors will most likely trigger the need to revise baseline estimates in most cases. In addition, reviewing the approach that was used in the baseline inventory provides useful information on how to estimate activity rates for this source group. Data on open burning is very limited at the country level, and expert judgment will be needed to fill such gaps. Checking the assumptions made in the baseline inventory to estimate activity rates and applying the same assumptions in the updated inventory equally enables obtaining consistent results and coherent trends in releases over time.

## Example Inventory 8 Source Group 7 Production and Use of Chemicals and Consumer Goods

### Introduction

The purpose of this case study is to illustrate the process of inventory development, update and revision, focusing on the production and use of chemicals. This case study provides a hypothetical inventory example of a Country X, including practical details on updating and revision of the inventory to assess trends in releases over time.

Country X developed the baseline inventory of dioxins in 2004 to support the development of the action plan as required by Article 5 of the Stockholm Convention. Activity data for the different sources of dioxins were collected for the reference year 2004 (baseline year). Activity data were obtained from the statistic yearbook. The inventory is developed by applying the Toolkit 2005 methodology and the emission factors specified in the 2005 edition of the Toolkit.

In this sample inventory, the inventory development process for the chemical industry is detailed, and provides useful guidance on estimating PCDD/PCDF releases for this source group.

### Baseline inventory for source category 7b

The baseline inventory of Country X was conducted in 2004 using data collected for the reference year 2004, according to the emission factors included in the Toolkit 2005 methodology.

#### Activity rates

For pentachlorophenol (PCP) and polychlorinated biphenyls (PCB), the production and use of PCP and PCB had been forbidden in Country X for many years, and thus no production of these chemicals occurred in the baseline year. For PCP-Na, the output was of 2,000 tons.

For chlorinated pesticides, 2,4,-dichlorophenoxy acetic acid (2,4-D) and 2,4,6-trichlorophenol were used as herbicides in Country X. The outputs of 2,4-D and 2,4,6-trichlorophenol in Country X in 2004 were of 16,000 and 800 tons respectively. No production of other chemicals listed in category 7b occurred in Country X in the baseline year 2004.

For chloranil, there were three plants in Country X in 2004. Plant A produced *p*-chloranil via chlorination of phenol. Plant B manufactured *p*-chloranil via hydroquinone, and Plant C produced *o*-chloranil via chlorination of phenol. The activity levels were of 300, 1,000, and 400 tons for Plants A, B, and C, respectively.

With regard to chlorobenzenes, the activity levels were of 6,000, 22,000 and 6,000 tons for *p*-dichlorobenzene, *o*-dichlorobenzene and 1,2,4-trichlorobenzene respectively.

In 2004, the production of alkali from the chlor-alkali industry in Country X was about 10.6 million tons. Among them, about 20,000 tons of alkali was produced using graphite anodes. The other alkali production in Country X was manufactured by membrane technology. No formation and emission of dioxins occurred during the production of chlorine/alkali by membrane technology.

The output of PVC was about 800,000 tons manufactured in modern plants (belonging to class 2 of EDC/VCM/PVC facilities) in Country X. About 4.53 million tons of PVC production belonged to class 3 (PVC only).

#### Estimation of dioxins from source 7b in Country X

Release estimates were made by assuming a linear relation between the intensity of the activity and the emission resulting from this activity.

##### Release to Air

For source 7b, the emission factors to air were only available for class 2 and 3 of the EDC/VCM/PVC in Toolkit 2005 methodology. Releases to air from source 7b were calculated by using the following equation:

$$\begin{aligned} & \text{Release of dioxins to air} \\ &= \sum_{i=1}^n \text{activity levels for class } i \times \text{emission factor to air for class } i \\ &= 800\,000 \text{ t} \times 0.4 \text{ } \mu\text{g TEQ/t (Modern plants, EDC/VCM or EDC/VCM/PVC)} + 4\,530\,000 \text{ t} \times \\ & \quad 0.0003 \text{ } \mu\text{g TEQ/t (PVC only)} \\ &= 0.32 \text{ g} \end{aligned}$$

##### Release to Water

For source 7b, the emission factors to water were only available for class 2 and 3 of the EDC/VCM/PVC in Toolkit 2005 methodology. Releases to water were calculated by using the following equation:

$$\begin{aligned} & \text{Release of dioxins to water} \\ &= \sum_{i=1}^n \text{activity levels for class } i \times \text{emission factor to water for class } i \\ &= 800\,000 \text{ t} \times 0.5 \text{ } \mu\text{g TEQ/t (Modern plants, EDC/VCM or EDC/VCM/PVC)} + 4\,530\,000 \text{ t} \times \\ & \quad 0.03 \text{ } \mu\text{g TEQ/t (PVC only)} \\ &= 0.536 \text{ g} \end{aligned}$$

##### Release to Land

Emission factors were not available for dioxin release into land in the Toolkit 2005 methodology. Thus, no release into the land was expected for source 7b according to the Toolkit 2005 methodology.

##### Release in Products

PCDD/PCDF releases in product were the dominant release route for source 7b. The emission of dioxins in product from source 7b was estimated to be 157.57 g according to the equation described below.

$$\begin{aligned} & \text{Release of dioxins in products} \\ &= \sum_{i=1}^n \text{activity levels for class } i \times \text{emission factor in products for class } i \\ &= 2\,000 \text{ t} \times 500 \text{ } \mu\text{g TEQ/t (PCP-Na)} + 800 \text{ t} \times 700 \text{ } \mu\text{g TEQ/t (2,4,6-trichlorophenol)} \end{aligned}$$

$$\begin{aligned}
 &+ 16\,000 \text{ t} \times 700 \text{ } \mu\text{g TEQ/t (2,4-D)} + 300 \text{ t} \times 400\,000 \text{ } \mu\text{g TEQ/t (p-chloranil via chlorination} \\
 &\text{of phenol)} + 1\,000 \text{ t} \times 100 \text{ } \mu\text{g TEQ/t (p-chloranil via hydroquinone)} + 400 \text{ t} \times 60\,000 \text{ } \mu\text{g} \\
 &\text{TEQ/t (o-chloranil via chlorination of phenol)} + 6\,000 \text{ t} \times 39 \text{ } \mu\text{g TEQ/t (p-} \\
 &\text{dichlorobenzene)} + 800\,000 \text{ t} \times 0.03 \text{ } \mu\text{g TEQ/t (Modern plants, EDC/VCM or} \\
 &\text{EDC/VCM/PVC)} + 4\,530\,000 \text{ t} \times 0.1 \text{ } \mu\text{g TEQ/t (PVC only)} \\
 &= 157.57 \text{ g}
 \end{aligned}$$

### Release in Residues

PCDD/PCDF releases in residues were significant in 2005. The emission factors of dioxins in residues from source 7b were available for production of chlorobenzenes, Chlorine/alkali, and EDC/VCM/PVC production according to the Toolkit 2005 methodology. Thus, the estimated release of PCDD/PCDF in residues from source 7b was of 46.91 g.

$$\begin{aligned}
 &\text{Release of dioxins in residues} \\
 &= \sum_{i=1}^n \text{activity levels for class } i \times \text{emission factor in residues for class } i \\
 &= 6\,000 \text{ t} \times 3\,000 \text{ } \mu\text{g TEQ/t (1,2,4-trichlorobenzene)} + 20\,000 \text{ t} \times 1\,000 \text{ } \mu\text{g TEQ/t (Chlor-} \\
 &\text{alkali production using graphite anodes)} + 800\,000 \text{ t} \times 10 \text{ } \mu\text{g TEQ/t (Modern plants,} \\
 &\text{EDC/VCM or EDC/VCM/PVC)} + 4\,530\,000 \text{ t} \times 0.2 \text{ } \mu\text{g TEQ/t (PVC only)} \\
 &= 46.91 \text{ g}
 \end{aligned}$$

The total dioxin release from source 7b by five different release routes was calculated to be 205.33 g. The emission inventory for source 7b is presented in the following table.

$$\text{Total dioxin release} = \text{Release to Air} + \text{Release to Water} + \text{Release to Land} + \text{Release in Products} + \text{Release in Residues} = 0.32 \text{ g} + 0.536 \text{ g} + 157.57 \text{ g} + 46.91 \text{ g} = 205.33 \text{ g}$$

### Baseline inventory (reference year 2004)

Class	Source category 7b	Production t/a	Annual release				
			g TEQ/a	g TEQ/a	g TEQ/a	g TEQ/a	g TEQ/a
	Production and Use of Chemicals		Air	Water	Land	Product	Residue
	<b>Chemical industry</b>		<b>0.321</b>	<b>0.536</b>		<b>157.571</b>	<b>46.906</b>
	<i>PCP</i>	2,000				<b>1.000</b>	
1	European, American production (chlorination of phenol with Cl <sub>2</sub> )	0				<b>0</b>	
2	Chinese production (thermolysis of HCH)	0				<b>0</b>	
3	PCP-Na	2,000				<b>1.000</b>	
	<i>PCB</i>	0				<b>0</b>	
1	Low chlorinated, e.g., Clophen A30, Aroclor 1242	0					
2	Medium chlorinated, e.g., Clophen A40, Aroclor 1248	0				<b>0</b>	
3	Medium chlorinated, e.g., Clophen A50, Aroclor 1254	0				<b>0</b>	
4	High chlorinated, e.g., Clophen A60, Aroclor 1260	0				<b>0</b>	
	<i>Chlorinated Pesticides</i>	16,800				<b>11.760</b>	

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1	Pure 2,4,5-Trichlorophenoxy acetic acid (2,4,5-T)	0				0		
2	2,4,6-Trichlorophenol	800				0.560		
3	Dichlorprop	0				0		
4	2,4-Dichlorophenoxy acetic acid (2,4-D)	16,000				11.200		
5	2,4,6-Trichlorophenyl-4'-nitrophenyl ether (CNP = chloronitrofen )	0				0		
	Old technology	0				0		
	New technology	0				0		
	<i>Chloranil</i>	1,700				144.100		
1	<i>p</i> -chloranil via chlorination of phenol	300				120.000		
2	<i>p</i> -chloranil via hydrochinone	1,000				0.100		
3	Dyestuffs on chloranil basis (old process, Class 1)	0				0		
4	<i>o</i> -chloranil via chlorination of phenol	400				24.000		
	<i>Chlorobenzenes</i>	34,000				0.234	18	
1	<i>p</i> -Dichlorobenzene	6,000				0.234		
2	<i>o</i> -Dichlorobenzene	22,000				NA		
3	1,2,4-Trichlorobenzene	6,000				NA	18	
	<i>Chlorine/chlor-alkali production</i>	20,000					20	
	Chlor-alkali production using graphite anodes	20,000					20	
	<i>ECD/VCM/PVC</i>	5,330,000	0.3	0.5		0.477	9	
1	Old technology, EDC/VCM, PVC	0		0				
2	Modern plants, EDC/VCM or EDC/VCM/PVC	800,000	0.32	0.400		0.024	8	
3	PVC only	4,530,000	0.0014	0.1359		0.453	0.9	
<b>Category 7b (Total per vector)</b>			<b>0.321</b>	<b>0.536</b>		<b>157.571</b>	<b>46.906</b>	
<b>Category 7b (Grand total)</b>			<b>205.33</b>					

### Update and revision of the inventory

The updated inventory of Country X was developed using data of activity levels collected for the reference year 2010, according to the updated emission factors in Toolkit 2013. The revised Toolkit includes important structural changes to the classification of sources in the chemical industry sector, new or revised emission factors for a number of sources, as well as additional source categories and classes.

The activity levels of chemicals production are the same as in the baseline year and the corresponding release estimates are summarized in the following table using the Toolkit 2013 and corresponding emission factors.

### Updated inventory (reference year 2010)

Class	Source categories	Production t/a	Annual release				
			g TEQ/a	g TEQ/a	g TEQ/a	g TEQ/a	g TEQ/a
<b>7b</b>	<b>Chlorinated Inorganic Chemicals</b>		0.0	0.0	0.0	0.0	20.0
	<i>Elemental chlorine production (per ton ECU)</i>	20'000	0	0	0	0	20
1	Chlor-alkali production using graphite anodes	20'000					20
2	Chlor-alkali production using titanium electrodes						



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2a	Low-End Technologies				0		0
2b	Mid-Range Technologies				0		0
2c	High-End Technologies				0		0
7c	<b>Chlorinated Aliphatic Chemicals</b> <i>EDC/VCM and EDC/VCM/PVC (per ton EDC)</i>		0.5	0.4	0.0	0.0	0.4
		800'000	0.040	0.400	0.000	0.000	0.076
1	Low-End Technologies						
1a	With fixed-bed oxychlorination catalyst		0.000	0.000		0.000	0.000
1b	With fluidized-bed oxychlorination catalyst		0.000	0.000		0.000	0.000
2	Mid-Range Technologies						
2a	With fixed-bed oxychlorination catalyst		0.000	0.000		0.000	0.000
2b	With fluidized-bed oxychlorination catalyst		0.000	0.000		0.000	0.000
3	High-End Technologies						
3a	With fixed-bed oxychlorination catalyst	800'000	0.040	0.400			0.076
3b	With fluidized-bed oxychlorination catalyst		0.000	0.000			0.000
	<i>PVC only (per ton PVC product)</i>	4'530'000	0.453	0.014	0.000	0.000	0.281
1	Low-End Technologies		0.000	0.000			0.000
2	Mid-Range Technologies	4'530'000	0.453	0.014			0.281
3	High-End Technologies		0.000	0.000			0.000
7d	<b>Chlorinated Aromatic Chemicals (per ton product)</b> <i>Chlorobenzenes</i>		0.0	0.0	0.0	455.4	0.0
		28'000	0.000	0.000	0.000	1.092	0.000
1	1,4-Dichlorobenzene	28'000				1.092	
	<i>PCB</i>	0	0.000	0.000	0.000	0.000	0.000
1	Low chlorinated, Clophen A30, Aroclor 1242					0.000	
2	Medium chlorinated, Clophen A40, Aroclor 1248					0.000	
3	Medium chlorinated, Clophen A50, Aroclor 1254					0.000	
4	High chlorinated, Clophen A60, Aroclor 1260					0.000	
	<i>PCP and PCP-Na</i>	2'000	0.000	0.000	0.000	25.000	0.000
1	PCP					0.000	
2	PCP-Na	2'000				25.000	
	<i>2,4,5-T and 2,4,6- trichlorophenol</i>	800	0.000	0.000	0.000	0.560	0.000
1	2,4,5-T					0.000	
2	2,4,6- trichlorophenol	800				0.560	
	<i>Chloronitrofen (CNP)</i>	0	0.000	0.000	0.000	0.000	0.000
1	Old technologies					0.000	
2	New technologies					0.000	
	<i>Pentachloronitrobenzene (PCNB)</i>	0	0.000	0.000	0.000	0.000	0.000
1	Low-End Technologies					0.000	
2	Mid-Range Technologies					0.000	
3	High-End Technologies					0.000	
	<i>2,4-D and derivatives</i>	16'000	0.000	0.000	0.000	2.720	0.000
1	Low-End Technologies					0.000	
2	Mid-Range Technologies	16'000				2.720	
3	High-End Technologies					0.000	
	<i>Chlorinated Paraffins</i>	0	0.000	0.000	0.000	0.000	0.000
1	Low-End Technologies						

2	Mid-Range Technologies					0.000	
3	High-End Technologies					0.000	
	<i>P-Chloranil</i>	2'000	0.000	0.000	0.000	1900.000	0.000
1	Direct chlorination of phenol	1'000				400.000	
2	Chlorination of hydroquinone with minimal purification					0.000	
3	Chlorination of hydroquinone with moderate purification	1'000				26.000	
4	Chlorination of hydroquinone with advanced purification					0.000	
	<i>Phthalocyanine dyes and pigments</i>	0	0.000	0.000	0.000	0.000	0.000
1	Phthalocyanine copper					0.000	
2	Phthalocyanine green					0.000	
	<i>Dioxazine dyes and pigments</i>	0	0.000	0.000	0.000	0.000	0.000
1	Blue 106					0.000	
2	Blue 108					0.000	
3	Violet 23					0.000	
	<i>Triclosan</i>	0	0.000	0.000	0.000	0.000	0.000
1	Low-End Technologies					0.000	0.000
2	Mid-Range Technologies					0.000	
3	High-End Technologies					0.000	
7e	<b>Other Chlorinated and Non-Chlorinated Chemical (per ton product)</b>		0.0	0.0	0.0	0.0	0.0
	<i>TiCl4 and TiO2</i>	0	0.000	0.000	0.000	0.000	0.000
1	Low-End Technologies			0.000		0.000	0.000
2	Mid-Range Technologies			0.000		0.000	0.000
	<i>Caprolactam</i>	0	0.000	0.000	0.000	0.000	0.000
1	Caprolactam		0.000	0.000			
<b>Chemicals Industry (categories 7b through 7e)</b>			<b>0.493</b>	<b>0.414</b>	<b>0.000</b>	<b>455.372</b>	<b>20.357</b>
<b>Chemicals Industry (Grand total)</b>			<b>476.635</b>				

Although the activity rates remained at constant rates since 2004, the difference between the baseline and updated releases is consequent:  $476.63 - 205.33 = 271.3$  g TEQ. In particular, releases in product are twice as high as baseline values. This is only due to the changes in the Toolkit emission factors, as the activity rates remained at constant levels since 2004. To ensure consistent results over time, the baseline release estimates need to be revised according to the Toolkit 2013 set of emission factors, ensuring that the difference between the 2010 and 2004 values is, as expected, null.

## Conclusion

New data and information have been integrated in the revised 2013 edition of the Toolkit, and important changes have been made to emission factors and the classification of sources for the chemical industry. The updating of the inventory for this source group needs to be accompanied by the revision of the baseline values to enable assessment of consistent trends in releases over time.

## Example Inventory 9 Source group 8 Miscellaneous

### I. Source category 8b Crematoria

This example inventory aims to illustrate the process of inventory development, update and revision for source group 8: Miscellaneous, source category 8b: Crematoria. This case study provides a hypothetical example of a country X that compiles inventory data for crematoria as part of the action plan within the National Implementation Plan (NIP) according to the Stockholm Convention on Persistent Organic Pollutants (POPs).

#### Baseline inventory

The baseline inventory of country X was conducted in 2005 by using data collected for 2004 (reference year); the amount of PCDD/PCDF releases to air and residue were calculated following the Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases, UNEP 2005. According to country X, cremation was mainly performed as a Buddhism tradition. Therefore, religion and death records were obtained from National Statistics in 2004, as well as the number and list of Buddhist temples that have cremation facilities. According to country X, 75.82% of deaths resulted in cremations. Questionnaires were sent to these temples to obtain more detailed information including the type and temperature of the burning chamber, as well as after burning chamber, duration of operation, dust abatement system, air pollution control system, type and amount of fuel, and number of cremations per year.

The crematoria were classified into 3 classes according to the technologies in use, based on the data obtained from questionnaires complemented by site visits as follows:

- Class 1 (no control) refers to the crematoria where the combustion temperature is below 850 °C, with uncontrolled combustion air flow or no flue gas cleaning system in place. The coffin is decorated with plastic material or made of treated wood;
- Class 2 (medium control) refers to the crematoria where the combustion temperature is above 850°C, with controlled combustion air flow and only dust removal in place. The coffin does not contain plastic material or treated wood;
- Class 3 (optimal control) refers to the crematoria where the combustion temperature is above 850°C with controlled combustion air flow and air pollution control system (APCS) in operation.

The data for Class 1, 2 and 3 are segregated, then the activity rate or production (t/a) of crematoria in each class is multiplied by a PCDD/PCDF emission factor to obtain the amount of PCDD/PCDF releases to air and residue as illustrated below:

	Source Categories	Activity (t/a)	Annual release (g I-TEQ/a)				
			Air	Water	Land	Product	Residue
	<b>8 Miscellaneous</b>						
	<b>8b Crematoria</b>						
1	No control	238,455	21.46				ND
2	Medium control	15,333	0.15				0.04
3	Optimal control	0	0.00				0.00

	<b>Total for Crematoria</b>	<b>253,788</b>	<b>21.61</b>	<b>0.00</b>	<b>0.00</b>	<b>0.00</b>	<b>0.04</b>
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### Updating of the inventory and revising the baseline

The measures included in the action plan targeting crematoria are based on best available techniques considering both environmental aspects (e.g. appropriate air pollution control systems) and technology (e.g. minimum temperature, residence time and oxygen content requirements). Further to implementing these measures, country X needs to assess whether PCDD/PCDF releases from this source decreased over time. The inventory is thus updated in 2011 to evaluate the changes in releases as a result of implementing best available techniques and best available practices. Data were collected for 2010 (reference year). During the process of updating the inventory it was found that 20 new crematoria with optimal control for PCDD/PCDF (class 3) release were installed in various regions in country X. Questionnaires were sent to both new and existing crematoria to obtain up-to-date information regarding their production or activity rates, temperature and duration of cremation process, fuel use, air pollution control system and evaluate/reclassify these facilities according to their current technology profile and activity levels. The same approach as in the baseline inventory was thus applied and resulted in 30% of the crematoria which were classified as class 1 in the baseline inventory being upgraded to class 2, and 5% of the crematoria which were classified as class 2 in the baseline being upgraded to class 3.

The results show that although the number of facilities increased in country X from 2004 to 2010, PCDD/PCDF releases decreased over the same period of time as a result of phasing in best available techniques for crematoria:

	Source Categories	Activity (t/a)	Annual release (g I-TEQ/a)				
			Air	Water	Land	Product	Residue
	<b>8) Miscellaneous</b>						
	<b>8b) Crematories</b>						
1	No control	99,000	8.91				ND
2	Medium control	152,000	1.52				0.38
3	Optimal control	50,000	0.02				0.12
	<b>Total for Crematoria</b>	<b>253,788</b>	<b>10.45</b>				<b>0.5</b>

Country X also plans an own PCDD/PCDF measurement campaign to collect and analyze samples from several facilities and refine the emission factors used in estimating releases. Once the emission data are generated and new emission factors derived, country X will revise the inventory by applying the same set of revised emission factors based on own measurements, to enable consistent evaluation of trends in releases over time.

### Conclusion

When updating the PCDD/PCDF inventory, it is necessary to review the baseline or previous inventories to maintain consistency over time and ensure that the estimates obtained are comparable over time. Data quality is important; therefore, it is also essential to revise and update data obtained from national statistics, questionnaires and site visits. More specifically, it is important to note all factors such as the

type of wood used in making the coffin, the preservatives used in treating the wood, plastic decorations added to the coffin, which would contribute to higher emissions of PCDD/PCDF to air and residue.

## II. Source category 8d Dry cleaning

### Introduction

Dioxin and furans emitted by the dry cleaning processes are found in the residues from distillation of the solvents and in filters. The emission factors for PCDD/PCDF found in the literature are usually expressed relative to the amount of residue from the solvent recycling process. Depending on the efficiency of stills, the bottoms range from a dry powder to a wet sludge that contains some solvent and the filtered material.

As shown in the Toolkit, a ton of residue from a dry cleaning machine may contain from 50 µg TEQ to 3000 µg TEQ of PCDD/PCDF depending on the nature of the cloths and tissues treated and the amount of contamination they contain.

To evaluate releases of PCDD/PCDF from the dry cleaning industry at a country level using the Toolkit method, one has to estimate the amount of residues generated and the relative nature of the tissues cleaned (heavy or contaminated textiles/normal textiles). In nearly all countries it is difficult to find such data to complete the inventory.

In case of lacking data, the following considerations may help in the estimation of these values:

- In a US EPA study, it was reported that an average dry cleaning machine (16 kg cloths per hour/1890 kg per month) generates an average of 183 kg of residues from the bottom of the still; an approximation of the amount of residues generated might be 1 kg/10 kg of textiles ;
- The ratio of heavy textiles to normal textiles treated in dry cleaning laundries is varying from country to country; an expert judgment is needed according to local practices;
- Last generation dry cleaning processes use less than 10 kg of solvent per ton of textiles;
- Residues of dry cleaning contain less than 1% of solvent (new dry cleaning processes).

### Example 1

In country A, the total installed dry cleaning capacity is 2500 kg/h and the activity is 3600 t/year of which 60% are heavy textiles. The total amount of residues is estimated at 360 t/year and the PCDD/PCDF releases in residues are:

- From heavy textiles :  $60\% \times 360 \text{ t/y} \times 3000 \text{ µg TEQ} = 0.648 \text{ g TEQ}$
- From light textiles :  $40\% \times 360 \text{ t/y} \times 50 \text{ µg TEQ} = 0.0072 \text{ g TEQ}$

Releases in residues for dry cleaning category are 0.6552 g TEQ/year. Total releases for this category are 0.6552 g TEQ/year as there is no release through other media.

### Example 2

In country B, there is not enough information concerning the production rate but we know there are at least 60 dry cleaning laundries in the country. We can assume the average production rate is 24,000

kg/year/laundry (1890 kg/month) and their release rate is 2.4 t/year. The ratio between the two categories of textiles treated is not really known but a local expert estimated that it would be about 1/1.

PCDD/PCDF releases in residues are:

- From heavy textiles :  $50\% \times 60 \times 2.4 \times 3,000 = 0.216 \text{ g TEQ}$
- From light textiles :  $50\% \times 60 \times 2.4 \times 50 = 0.0036 \text{ g TEQ}$

Total releases for dry cleaning category are 0.2196 g TEQ

### Example 3

In country C, there is no data concerning the production rate and the residues generation for the dry cleaning category, but it is known, from official statistics, that the average annual imported quantities of solvent for use in dry cleaning (perchloroethylene, Stoddard solvent, other brand names) are stable at about 500 tons per year.<sup>32</sup> Assuming an average consumption of 10kg/ton of textiles<sup>33</sup> treated in dry cleaning processes, a production rate of about 50 000 t is estimated, which will generate about 500 tons of residue.

PCDD/PCDF releases in residues are:

- From heavy textiles:  $50\% \times 500 \text{ t/y} \times 3,000 \mu\text{g TEQ} = 0.75 \text{ g TEQ}$
- From light textiles:  $50\% \times 500 \text{ t/y} \times 50 \mu\text{g TEQ} = 0.0125 \text{ g TEQ}$

Total PCDD/PCDF releases from dry cleaning are of 0.7625 g TEQ.

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<sup>32</sup> In addition to dry cleaning, are other possible uses of these solvents are possible, such as metal degreasing. It is thus important to try to obtain an industry-based breakdown of the import data.

<sup>33</sup> The regulation in US and Canada sets a limit of solvent consumption for dry cleaning to 6.5 l/ton of cloths (10 kg/ton of cloths in the case of perchlorethylene).

## Example Inventory 10 Source Group 9 Disposal and Landfill

### Baseline inventory

Country A has prepared its PCDD/PCDF inventory for the reference year 2005. For source group 9, data on the amount of wastes deposited on landfills and waste dumps, sewage collection, treatment and disposal were obtained from the National Department of Statistics and from the National Survey on Basic Sanitation, complemented by data from agencies and companies responsible for waste and sewage collection, treatment and disposal.

### Category 9a Landfills and Waste Dumps

To estimate leachate releases generated by organic decomposition of municipal solid waste, the total amount of wastes disposed of in sanitary landfills - 1,011,780 t/year - and in waste dumps – 809,424 t/year – was considered, resulting in a total of 1,821,204 t wastes disposed of per year. Reliable studies were conducted by researchers at the National University in Country A, indicating generation of leachate from 0.1 to 0.2 cubic meter per ton of waste disposed of. Considering the intermediate value of 0.15 m<sup>3</sup>/t, the total volume of leachate generated in 2005 was of 273,181,000 liters.

Information for the calculation of leachate from hazardous waste releases does not exist. The surveyed companies reported that formation of leachate in landfills containing industrial hazardous waste is small, as special landfills are used for this type of waste, compliant with the legislation in force, with low amounts of degradable organic matter, and where rain is prevented from reaching the landfilled waste.

Municipal solid wastes are considered to contain 5% of hazardous wastes according to information given by the Federal Environment Agency. The total annual release was then calculated by multiplying the activity rates by the corresponding emission factors according to the Toolkit (2005). The results are shown in the following table:

### Annual PCDD/PCDF releases for source category 9a (reference year 2005)

Category	Class	Activity Rate	Annual release (g TEQ/a)					Total
			Air	Water	Land	Product	Residue	
Landfills and waste dumps	Hazardous wastes	13,659,000 L/year leachate 91,060 t/year solid waste	-	0.003	-	-	4.6	14.9
	Non-hazardous wastes	259,521,600 L/year leachate 1,730,144 t/year solid waste	-	0.008	-	-	10.4	

### Landfill mining and excavation

Landfill mining and excavation was not considered in the baseline inventory of Country A. Nonetheless a good example of emission from this source is given by Torres *et al.* (2012). It is the case of a company in Sao Paulo that produced acetylene/vinylchloride monomer (VCM), ethylenedichloride (EDC) and PVC since mid 1950s and deposited the related production wastes on a landfill. The VCM production via the acetylene method stopped in 1996. The corporate landfill has been used for approximately 40 years and was closed in 1996. Lime milk from the acetylene process was the main type of waste disposed of at this site, with approximately 1,400,000 tons of lime milk stored (Torres *et al.* 2012). In 1997, a company started to mine the lime waste from the site and put it on the construction market for neutralizing citrus pulp to produce citrus pulp pellets (CPP). The citrus pulp pellets were exported to Europe as feed for cattle, resulting in PCDD/PCDF contamination of milk and dairy products in several countries (Malisch 2000, Torres *et al.* 2012). After the PCDD/PCDF contamination was discovered, mining of the PCDD/PCDF contaminated lime for CPP ceased. To evaluate the extent and type of PCDD/PCDF contamination of the landfill, 323 samples were taken from the site and analyzed. Concentrations ranged between 0 to 81,000 ng TEQ/kg, averaging around 1000 ng TEQ/kg. The total TEQ amount at the site was estimated at 1.4 kg TEQ. Patterns in the higher contaminated samples (1000 ng – 81,000 ng TEQ/kg) were similar to the EDC catalysts described by Carroll *et al.* (2001). During the last ten years, securing measures were installed including the construction of a hydraulic barrier. The site was also capped (Torres *et al.* 2012). This example demonstrates how PCDD/PCDF from reservoirs can enter via landfill mining in the food chain, directly into cattle feed and human nutrition.

#### Category 9b Sewage and Sewage Treatment

The National Statistics Department detains information on the volume and type of disposal and treatment given to sewage collected in Country A. The volume of sewage collected and treated was of 668,000 m<sup>3</sup>/day (243,820,000 m<sup>3</sup>/year). The amount of sludge generated in several types of treatment processes was of 175 g/m<sup>3</sup> (calculated on the basis of 25 grams of dry sludge per person per day and a daily consumption of water of 0.143 m<sup>3</sup>/person).

It was estimated that 10% of the sewage collected (24,382,000 m<sup>3</sup>/year) contains industrial effluents with chlorine relevance; sewage treatment processes generate sludge, which is afterwards removed. The remaining 90% of the sewage collected (219,438,000 m<sup>3</sup>/year) are treated in systems with (93%) and without (7%) sludge removal. Treatment systems without removal of sludge are of the wetland type.

No statistics were available to calculate the activity rates for remote environments or with input control, and they were not included in the inventory.

The results of the inventory are shown in the following table:

#### Annual PCDD/PCDF releases for source category 9b (reference year 2005)

Category	Class	Activity Rate	Condition	Annual release (g TEQ/a)					Total
				Air	Water	Land	Product	Residue	
Sewage and	Mixed domestic and	0.0	No sludge removal	-	0.0			0.0	8.0



sewage treatment	industrial inputs	Sewage: 24,382,000 m <sup>3</sup> /year Sludge: 4,267 t/year	With sludge removal	-	0.012			4.27	
	Urban environments	Sewage: 15,360,660 m <sup>3</sup> /year	No sludge removal	-	0.031			0.0	
		Sewage: 204,077,340 m <sup>3</sup> /year Sludge: 35,714 t/year	With sludge removal	-	0.102			3.57	
	Remote environments or input control	N/A							

### Category 9c Open Water Dumping

Water consumption in urban areas reached a total amount of 971,000 m<sup>3</sup>/day in 2005, producing 873,900 m<sup>3</sup> sewage/day. By discounting the volume of sewage collected and treated (668,000 m<sup>3</sup>/day), it was calculated that the amount dumped in open water (mainly rivers and ocean) was of 205,900 m<sup>3</sup>/day or 75,153,500 m<sup>3</sup>/year. The same consideration was made in relation to the presence of industrial effluents. Thus, the activity rate in class 1 will be 10% of total sewage volume discharged in open water, and the remaining 90% is assigned to class 2. No information was collected on class 3 (remote environments or input control).

### Annual PCDD/PCDF releases for source category 9c (reference year 2005)

Category	Class	Activity Rate	Annual release (g TEQ/a)					Total
			Air	Water	Land	Product	Residue	
Open Water Dumping	Mixed domestic and industrial inputs	7,515,350 m <sup>3</sup> /year	-	0.038	-	-	-	0.051
	Urban environments	67,638,150 m <sup>3</sup> /year	-	0.014	-	-	-	
	Remote environments	N/A						

### Category 9d Composting

Composting is not a relevant way of disposing of waste in Country A, and estimates of amounts of wastes converted to compost are uncertain. About 1% of municipal waste is considered to be converted

in compost, that is, around 20,000 t/year. Considering the default value of 30% of water content given in the Toolkit (2005), the total amount of compost produced would be 14,000 t/year (dry basis). Assuming an all organic fraction in compost, annual releases of PCDD/PCDF are of 1.4 g TEQ/year.

#### Category 9e Waste Oil Treatment (Non-Thermal)

As there is no emission factor for this type of source, no further attempt was made to quantify PCDD/PCDF releases from this source.

#### Total Annual Releases from Source Group 9

The total annual releases of PCDD/PCDF from source group 9 in Country A, in the reference year 2005, amount to 24.4 g TEQ/year.

#### Updating of the inventory

Based upon the results of 2005 baseline inventory, Country A introduced a number of measures to reduce releases of PCDD/PCDF. In relation to source group 9, the main actions taken were:

- a) To reduce by 50% the hazardous content of wastes deposited on landfills and dumps;
- b) To introduce a recycling program to reduce the amount of landfilled waste per capita. In 2010 the reduction was of 5%;
- c) To eliminate mixing of industrial inputs into sewage collection and treatment systems.

The update of the inventory is described below.

#### Category 9a Landfills and Waste Dumps

The same methodology as in the baseline inventory was employed to estimate releases generated by organic decomposition of municipal solid waste. According to the Toolkit 2013, emission factors for category 9a have been revised and the need to estimate the amount of leachate generated by waste decomposition has been eliminated; the emission factors are now based on the amount of solid wastes generated. Also, as a result of measures taken, hazardous wastes contained in domestic wastes reduced by half and there was a 5% reduction on domestic wastes.

The updated values are shown in the table below. The results show a decrease of 6.4 g TEQ/year, as compared with the baseline release estimates.

#### Annual PCDD/PCDF releases for source category 9a (reference year 2010)

Category	Class	Activity Rate	Annual release (g TEQ/a)					Total
			Air	Water	Land	Product	Residue	
Landfills and waste dumps	Hazardous wastes	45,530 t/year	-	0.2	-	-	NA	8.5
	Mixed wastes	-	-	-	-	-		
	Domestic wastes	1,643,637 t/year	-	0.08	-	-	8.2	

### Category 9b Sewage and Sewage Treatment

The data from the National Statistics Department show that the sewage volume decreased by 10% due to the elimination of mixed industrial and domestic effluents in relation to 2005. The type of disposal and treatment remained the same as in 2005. Then the volume of sewage collected and treated was of 601,200 m<sup>3</sup>/day (219,438,000 m<sup>3</sup>/year). The amount of sludge generated in several types of treatment processes in use in Country A was thus similarly estimated as in 2005.

However, based on the measures included in the National Implementation Plan (NIP) of Country A, there is no mixing of industrial inputs with chlorine relevance. All sewage collected can be classified as class 2, 93% being treated in systems with sludge removal and 7% in systems without sludge removal.

No statistics were available to calculate the activity rates for remote environments or with input control, and they were not included in the inventory.

The total annual releases for 2010 show a reduction of 7.14 g TEQ/year as compared with the baseline situation.

#### Annual PCDD/PCDF releases for source category 9b (reference year 2010)

Category	Class	Activity Rate	Condition	Annual release (g TEQ/a)					Total
				Air	Water	Land	Product	Residue	
Sewage and sewage treatment	Mixed domestic and specific industrial inputs	0.0	No sludge removal	-	0.0			0.0	0.7
		0.0	With sludge removal	-	0.0			0.0	
	Urban and industrial inputs	Sewage: 13,824,594 m <sup>3</sup> /year	No sludge removal	-	0.01			0.0	
		Sewage: 183,669,606 m <sup>3</sup> /year Sludge: 32,142 t/year	With sludge removal	-	0.04			0.64	
	Domestic inputs	N/A	No sludge removal						
			With sludge removal						

### Category 9c Open Water Dumping

Water consumption in urban areas registered a 10% reduction in relation to 2005 consumption, due to the separation of industrial effluents with chlorine relevance from domestic effluents, reaching a volume of 873,900 m<sup>3</sup>/day, producing a total amount of sewage of 786,510 m<sup>3</sup>/day. By discounting the volume of sewage collected and treated (601,200 m<sup>3</sup>/day), the amount dumped in open water (rivers and

ocean) was estimated at 185,310 m<sup>3</sup>/day or 67,638,150 m<sup>3</sup>/year. This is entirely assigned to class 2. There is no information on class 3 (remote environments or input control). The total annual releases for category 9c in 2010 (0.014 g TEQ/year) are thus lower than 2005 releases (0.051 g TEQ/year).

#### Category 9d Composting

The situation in 2010 changed due to changes in the Toolkit 2013 emission factors. The amount of wastes converted to compost remained the same and is assigned to class 1 (compost of organic wastes separated from mixed wastes). The release decreased by 50%, with a total of 0.7 g TEQ/year of PCDD/PCDF.

#### Category 9e – Waste Oil Treatment (Non-Thermal)

No releases are calculated for this source category, similarly as in 2005.

#### Total Annual Releases on Source Group 9

The total annual releases of PCDD/PCDF from source group 9 in Country A, in the reference year 2010, amounts to 9.9 g TEQ/year, registering thus a decrease of 14.4 g TEQ/year as compared to the baseline.

#### Revision of the Baseline Inventory

The update of the inventory for the reference year 2010 was associated with changes in the Toolkit emission factors. Thus, to be able to calculate trends in releases over time based on a consistent set of emission factors, the baseline values must be recalculated by using the Toolkit 2013. The revision of the baseline inventory enabled the detection of a decreasing trend in releases from 2004 to 2010.

#### Category 9a Landfills and Waste Dumps

##### Annual PCDD/PCDF releases for source category 9a (revised for the reference year 2005)

Category	Class	Activity Rate	Annual release (g TEQ/a)					Total
			Air	Water	Land	Product	Residue	
Landfills and waste dumps	Hazardous wastes	91,060 t/year solid waste	-	0.5	-	-	NA	9.2
	Mixed wastes	0	-	-	-	-	-	
	Domestic wastes	1,730,144 t/year solid waste	-	0.1	-	-	8.7	

#### Category 9b Sewage and Sewage Treatment

##### Annual PCDD/PCDF releases for source category 9b (reference year 2005)

Category	Class	Activity Rate	Condition	Annual release (g TEQ/a)					Total
				Air	Water	Land	Product	Residue	

Sewage and sewage treatment	Mixed domestic and industrial inputs	N/A	No sludge removal	-	0.0			0.0	<b>0.9</b>
		Sewage: 24,382,000 m <sup>3</sup> /year Sludge: 4,267 t/year	With sludge removal	-	0.024			0.85	
	Urban and industrial inputs	Sewage: 15,360,660 m <sup>3</sup> /year	No sludge removal	-	0.015			0.0	
		Sewage: 204,077,340 m <sup>3</sup> /year Sludge: 35,714 t/year	With sludge removal	-	0.04			0.7	
	Domestic inputs	N/A	No sludge removal						
			With sludge removal						

For categories 9c Open Water Dumping, and 9e Waste Oil Treatment, no changes in emission factors have been made in the revised Toolkit, therefore there is no impact on the calculation of release estimates for these sources. The inventory does not need to be revised in such cases where both the emission factors and the activity rates remain unchanged as compared with the baseline.

For category 9d Composting, the releases are revised to account for the changes in emission factors. The revised PCDD/PCDF release estimates amount to 0.7 g TEQ/year.

#### **Comparison of total releases for reference year 2010 to the revised baseline inventory**

The total annual releases of PCDD/PCDF from source group 9 in Country A, in the reference year 2010, amounts to 10 g TEQ, and 12 g TEQ in the revised baseline inventory for reference year 2005, registering a reduction of 2 g TEQ, or around 15%. The results show the importance of the revision of baseline inventory, since without this step the conclusion after updating the inventory would have been a reduction of about 13 g TEQ, or around 60%.

## Example inventory 11      Source Group 10 Contaminated Sites and Hotspots

This example inventory contains a series of practical examples and best practice cases of PCDD/PCDF inventories for the most relevant source categories, including, where available, quantitative PCDD/PCDF data.

### 10a Production Sites of Chlorine

#### I. Chlor-alkali production

Experience from China, Germany, Sweden and the USA proves that chlor-alkali processes can generate large quantities of PCDD/PCDF (Weber *et al.* 2008). Limited data are available on the total PCDD/PCDF production and release in chlor-alkali plants, but a detailed inventory has been prepared and published for Rheinfelden in Germany (Otto *et al.* 2006). Griesheim Elektron operated a chlor-alkali plant at this site starting with 1898 for 87 years. Toxic residues of the chlor-alkali process together with other industrial waste were disposed of in small gravel pits in the vicinity of the plant without safety measures. In 1989, widespread PCDD/PCDF contamination was discovered in soils (Otto *et al.* 2006). The analysis demonstrated that PCDF contamination was dominant, and samples revealed peak concentrations of 26,000 ng TEQ/kg in topsoil and up to 3,800,000 ng TEQ/kg in deep soil, comprising mainly of historic sludge deposits.

The approach for the inventory at Rheinfelden included:

- An investigation of the history of chlorine production and technologies used at the factory and a review of the methods and sites used for the disposal of residues.
- A preliminary screening of contamination: in a first phase, 100 locations were sampled with 303 core probes. Forty representative pooled samples were then analysed for PCDD/PCDF, heavy metals, total organics and other site-specific parameters.
- In the second phase it was discovered that heavily contaminated solid residues have been used as infill materials at many sites as the city developed in the 20th century. This resulted in widespread contamination with PCDD/PCDF, heavy metals and other contaminants. The entire inner city area (ca. 290 ha) was assessed. Soil samples from 1615 estates involving 3566 individual drillings were collected and screened. Finally, a soil contamination map of the entire city was developed, showing indicator heavy metals.

A PCDD/PCDF inventory was established based on monitoring data and related assessments, followed by remediation and containment of deposits and contaminated soils. The total amount of PCDD/PCDF residues deposited from the chlor-alkali plant was estimated at 8.5 kg I-TEQ (Otto *et al.* 2006). Furthermore, between 1970 and 1986 the factory also produced PCP and PCP-Na, and the residues associated with this production were estimated to contain an additional 7.7 kg I-TEQ (with a total 7 tons of PCDD/PCDF), thus a total PCDD/PCDF contamination of 16.2 kg I-TEQ (Otto *et al.* 2006).

#### II. Former Leblanc factory site

The only PCDD/PCDF inventory yet established for a Leblanc factory is at Lampertheim, Germany, for a plant which operated between 1840 and 1893. In the late 1980s, high levels of arsenic and lead were detected in soil in the vicinity of the site. Subsequent investigations in the 1990s also revealed high levels of PCDF (and PCDD to a lesser extent) (Balzer *et al.* 2007, 2008).

The assessment included historical investigation and archive research to retrieve information on the production site, as well as technical and scientific literature review on the Leblanc process and associated processes. Based on these investigations, a detailed soil analysis was undertaken, with more than 600 soil cores analysed for a range of organic and inorganic contaminants. Approximately 500 samples were also analysed for PCDD/PCDF, confirming that the entire surface and subsurface soil was highly contaminated with PCDD/PCDF and heavy metals. A PCDD/PCDF inventory was thus established based on the levels measured in samples and the volumes of deposited residues and contaminated soils. The total amount of PCDD/PCDF in soils and deposits was of 1-10 kg TEQ, while the total arsenic and lead contamination was of 12- 80 tons and 50-300 tons respectively (Balzer *et al.* 2007).

Since a range of chemical processes were employed in Leblanc plants, the individual steps and processes were evaluated with respect to their PCDD/PCDF formation potential. Four distinct operational steps with a high PCDD/PCDF formation potential have been identified for the Lampertheim factory (Balzer *et al.* 2008):

- a) The direct manganese oxide method was used for chlorine production from HCl.
- b) The production of calcium hypochlorite (bleaching powder) from elemental chlorine and  $\text{Ca(OH)}_2$  in "chlorine chambers": in these processes, coal tar was used as a filler and protection material, resulting in PCDD/PCDF formation. At Lampertheim, highly contaminated residues with TEQ levels above 200  $\mu\text{g TEQ/kg}$  and waste deposits with levels of 500  $\mu\text{g TEQ/kg}$  were found in the vicinity of the former production area. The PCDD/PCDF pattern of these residues is similar to those characteristic of the chlor-alkali process.
- c) Hydrochloric acid released from the Leblanc process ovens was condensed in coke towers for further processing. PCDD/PCDF contamination in soils where the piping system and the coke towers were located was above 10  $\mu\text{g TEQ/kg}$ .
- d) Finally, the production of sodium sulphate and sal soda in "sulphate ovens" and flame ovens, with residues from these thermal processes contaminated with up to 95 ng TEQ/kg.

A European survey of Leblanc factories revealed that at least 70 to 100 factories were operated during the 19th century mainly in Great Britain, France and Germany (Balzer *et al.* 2008). According to historical records, 413,000 tons of sal soda were produced in 1865 via the Leblanc process, with the main producers located in the United Kingdom (234,000 tons), France (108,000 tons) and Germany (66,000 tons). An inventory of former Leblanc sites has only been made in Germany, where 15 locations have been identified (Balzer *et al.* 2008). At least 30 Leblanc factories have also been operated in France, while in the United Kingdom approximately 30 to 40 Leblanc factories were operational during the mid-19th century.

## **10b Production Sites of Chlorinated Organics**

## I. Chlorophenol production

The Finnish Environment Institute has compiled an inventory and risk assessment of PCDD/PCDF contaminated sediments from releases of a polychlorophenol (PxCp) wood preservative Ky-5. Ky-5 was manufactured in the upper reaches of the Kymijoki river in South-Eastern Finland between 1940 and 1984 (Verta *et al.* 2009).

The product consisted mainly of 2,3,4,6-tetrachlorophenol (83%), pentachlorophenol (8%) and 2,4,6-trichlorophenol (6%). PCDD/PCDF, especially the higher chlorinated dibenzofurans, were major impurities in the product and in residues. The company discharged residues into the river system resulting in highly contaminated sediments with a maximum PCDD/PCDF concentration above 400,000 µg/kg (Verta *et al.* 1999c).

Sediment cores from 220 sites were collected between 1997 and 2003. PCDD/PCDF were analysed from sub-samples of ten sediment cores, 35 surface sediment samples, 15 locations in the river and ten coastal sites from the Gulf of Finland (Isosaari *et al.* 2002, Verta *et al.* 2007).

Figure III.11.1 shows the concentration of PCDD/PCDFs in sediments. The total volume of contaminated sediments was estimated to be  $5 \times 10^6 \text{ m}^3$  and the hotspot volume amounted to approximately 90,000  $\text{m}^3$  of sediments with extremely high concentrations (max. 292,000 µg/kg or 1,060 µg I-TEQ/kg d.w.). These were located immediately downstream from the factory.

The total amount of Ky-5 chlorophenol-derived PCDD/PCDF was estimated to be approximately 5,960 kg (17.3 kg I-TEQ) in the river sediments and 1,770 kg (12.4 kg I-TEQ) in the Gulf of Finland (Fig. III.11.1; Verta *et al.* 2009). In addition to the PCDD/PCDF inventory, the Finnish Environment Institute calculated the yearly PCDD/PCDF fluxes within the river and into the Gulf of Finland and projections for the next decades (Verta *et al.* 2009).

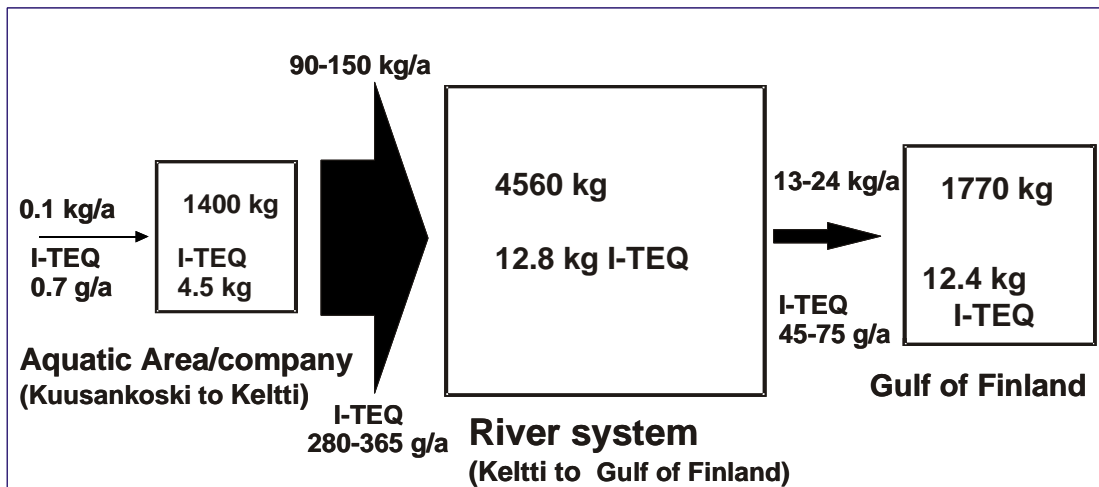


Figure III.11.1 2001 PCDD/PCDF inventory of the Kymijoki river and annual transport to the Gulf of Finland

## II. Lindane production with recycling of HCH waste isomers



In some cases, lindane production has recycled (part of) HCH waste isomers due to economic reasons and to reduce dumping of HCH waste. In Germany, HCH waste isomers were recycled between 1953 and 1984 by thermal decomposition (250°C-260°C) to produce technical tri/tetrachlorobenzene. In this reaction step, a so-called ‘decomposer residue’ was produced, containing 1.4 to 2.7% PCDD/PCDF with I-TEQ in the high ppm range (90 to 230 ppm) (Vijgen *et al.* 2011). The final residues from the HCH recycling process were highly contaminated with PCDD/PCDF and resulted in the closure of the factory in 1984 (Vijgen *et al.* 2011, Götz *et al.* 2012).

The total amount of PCDD/PCDF landfilled from registered waste residues generated by thermal HCH decomposition was estimated between 53 and 102 tons for sum PCDD/PCDF, and between 333 and 854 kg I-TEQ contained in approximately 3,700 tons of wastes from HCH recycling (Götz *et al.* 2012). In addition, approximately 2,500 tons of un-recycled HCH waste isomers and 10,000 tons of other organochlorine wastes with lower PCDD/PCDF content were deposited in at least eight landfills (Bürgerschaft Hamburg 1985, University Bayreuth 1995). A detailed inventory of contaminated sites and deposits has been developed for the city of Hamburg and other landfills. PCDD/PCDF fingerprinting has been used for assigning contamination and proving that a site was contaminated with PCDD/PCDF (Sievers and Friesel 1989).

- For the production site, a PCDD/PCDF inventory in the soil has been compiled (Table III.11.1). The site has been secured with a 50 m deep cut-off wall, groundwater was pumped and residues were incinerated (Weber and Varbelow 2012).
- At the Georgswerder landfill in Hamburg, approximately 50% of the PCDD/PCDF load (157-403 kg I-TEQ) contained in 1,750 tons of HCH ‘decomposer residues’ and 4,000 tons of other organochlorine waste were deposited (Götz *et al.* 2012). The landfill has been secured and oily leachates containing PCDD/PCDF were incinerated.
- Another deposit in Hamburg has also received waste from this factory and has been assessed and inventoried (Sievers and Friesel 1989).
- Approximately 50% of the PCDD/PCDF wastes (included in the inventory) were disposed of at six landfills outside Hamburg along with approximately 70% of the wastes. Detailed data on the leachate and groundwater situation from these individual landfills are not available.

Recycling of HCH waste has been undertaken by several other lindane producers (Vijgen *et al.* 2011) and may still be in practice today in two former lindane factories in India (Jit *et al.* 2010). A similar approach to establishing an inventory might be useful for other sites.

**Table III.11.1 PCDD/PCDF and other chlorinated organohalogen compounds in soil from storage, spills and leaks at the production site\***

Contaminant	Amount of organohalogen
Total PCDD/PCDF (TEQ)	6 kg
HCH isomers	262 tons
Chlorobenzenes	551 tons
Chlorophenols	18 tons

EOX (calculated to Cl)	663 tons
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\*contained in a total volume of 559,000 m<sup>3</sup> soil

### III. Other chemicals known or suspected to contain PCDD/PCDF or other unintentional POPs

While the levels of PCDD/PCDF in some products (*e.g.* pesticides) have been monitored, the levels in production residues are often unknown. To assess occupational safety during the excavation of the Bonfol chemical landfill in Switzerland, a PCDD/PCDF inventory of the deposited waste was compiled. The Basel Chemical Industry<sup>34</sup> (BCI) has produced and used a range of chlorinated aromatic compounds not known to be highly contaminated with PCDD/PCDF or precursors (*e.g.* 2,4-D, 2,4,5-T or PCP). Between 1961 and 1976, the industry disposed of 114,000 tons of chemical wastes in the Bonfol landfill, an old clay quarry. Because the landfill contaminated groundwater, BCI was forced to fully remediate the site by excavating and incinerating chemical wastes.

For the inventory, the chemicals listed by the German Environmental Agency (UBA) as containing or potentially containing PCDD/PCDF were used as one information source (UBA 1985). This list was supplemented by additional literature on substances containing PCDD/PCDF and PCB (Forster 2005, 2006) including:

- Three lists containing approximately 5,000 substances which were produced during 1960-2003, by BCI. The information included data on educts, production intermediates and products.
- Other unpublished internal documents from chemical companies including information on production and synthesis methods, capacity calculations and internal analysis reports.
- Newsletters and reports or other publications by companies, chemical associations and further publications.
- Analytical results available from samples taken from around disposal sites used by BCI members operating in Switzerland, France, Germany and the USA.
- The amended lists and additional information were then discussed with chemists, chemical engineers and laboratory experts at Roche, Sandoz, Geigy, Ciba and Ciba-Geigy.

It was established that at least 38 substances produced and used from the 1950s to 1970s by BCI contained, or potentially contained PCDD/PCDF. These substances were used in the production of several hundred final products. PCDD/PCDF wastes were estimated for four of these products: the production of trichlorophenol by Roche and the production of dioxazin pigments and paints, Mitin LA and triclosan by Geigy or Ciba-Geigy (Forster 2005, 2006) (Table III.11.2).

The majority of PCDD/PCDF and PCB impurities from educts and those formed during the production of trichlorophenol, triclosan, Mitin LA and Oxazin/Dioxazin pigments and paints ultimately ended up, by a process of filtration and distillation of the chlorinated solvents, in the residues and were ultimately disposed of at the Bonfol chemical landfill between 1965 and 1975. Considering the PCDD/PCDF quantities resulting from these four production processes, and taking into account that BCI was a heavy user of chlorinated solvents, it was shown that total TEQ levels of several tens of kilogram were present

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<sup>34</sup> <http://www.bci-info.ch/>

in the Bonfol landfill (Forter 2005, 2006). The total quantity of PCDD/PCDF and PCB was estimated to be as much as one ton (Forter 2005, 2006).

**Table III.11.2 Order of magnitude estimates of the PCDD/PCDF wastes from BCI production during 1964-1975**

Production/ use of	Period of time	Estimated total PCDD/PCDF amount (kg)	Estimated PCDD/PCDF I-TEQ (kg)
Trichlorophenol	End 1960s	Unknown	> 0.1
Oxazin & Dioxazin pigments and dyes	1965–1975	Several 100	1 to several kg
Triclosan	1966–1975	Several 10 to several 100	0.1 to 1
Mitin LA	1974–1975	Unknown	0.01 to several 0.01
<b>Total</b>		<b>Several 100</b>	<b>1 to several kg</b>

#### IV. Unintentionally produced HCB wastes from solvent production

Wastes from the production of chlorinated solvents at the former Kalush Chemical and Metallurgical Industrial Complex were buried near Kalush City, Ukraine. The solvents produced included carbon tetrachloride, tetrachloroethene and dichloroethene (ethylene dichloride EDC) for PVC manufacturing. Solvent production started in 1973 with an estimated production capacity of approximately 30,000 tons per year. Approximately 540 tons of hazardous “HCB waste” with unintentionally produced HCB as a primary contaminant was produced annually, suggesting an emission factor of 18 kg “HCB waste”/t solvent produced for this factory (Weber *et al.* 2011). The total amount of “HCB waste” deposited was estimated to be approximately 11,000 tons (UNEP, OCHA and EU Commission 2010). Since the HCB content of the waste is around 20%, the total amount of HCB deposited at this site can be estimated to be around 2,200 tons (Jacoff *et al.* 1986). Sampling of “HCB waste” also found PeCB at levels approximately an order of magnitude lower than HCB. The total quantity of PeCB waste contained in the total 11,000 tons of “HCB waste” can be estimated to be approximately 200 tons.

Other cases of stored or deposited HCB waste show that the inventories for solvent production facilities which did not have adequate destruction capacity in the 1950s to 1990s are of the same order of magnitude:

- The manufacture of chlorinated solvents by Orica between 1963 and 1991 produced more than 10,000 tons of concentrated “HCB waste” (Independent Review Panel 2006) ([www.oricabotanytransformation.com](http://www.oricabotanytransformation.com)). About 1,000 tons of this waste was generated by the production of ethylene dichloride (EDC) for manufacturing PVC.
- 80,000 drums of “HCB waste” were disposed of from Spolchemie (Chabaiovice, Czech Republic) near the Elbe river (Heinisch *et al.* 2006). Subsequent leaching of the waste into the Elbe river resulted in high concentrations of HCB accumulating in downstream sediments and PeCB levels of approximately 15% of those of HCB (Heinisch *et al.* 2006).

#### V. Lindane production

In the production of lindane (gamma-HCH), approximately 85% of the waste isomers are formed in the chlorination step of benzene as unintentional POPs (Vijgen *et al.* 2011). The active gamma-isomer was commonly separated, and the remaining 85 to 90% waste isomers, consisting mainly of alpha-HCH and some beta, delta and epsilon-HCH, were dumped. A global inventory of these wastes was compiled based on information collected for over 20 years of production, including HCH production capacities and estimated amounts of wastes generated (Vijgen *et al.* 2011). 1.6 – 1.9 million tons of disposed HCH waste were thus estimated in the former producing countries (Albania, Austria, Argentina, Brazil, China, Croatia, Czech Republic, France, Germany (including former German Democratic Republic), Hungary, India, Italy, Japan, Macedonia (former Yugoslavia), Nigeria, Poland, Romania, Slovakia, South Africa, Spain, Switzerland, Turkey, The Netherlands, UK, USA, and the former USSR). This inventory is considered to underestimate the scale of the problem because of the incomplete reporting and the likely existence of unidentified production sites and waste deposits.

In a second inventory approach, the total quantity of HCH waste was estimated by using the proportion of waste isomers produced per tonne of lindane used (Vijgen *et al.* 2011). Global historical lindane use for agricultural purposes was estimated to have been between 1950 and 2000 of 450,000 t, with the largest share (63%) in Europe (Vijgen *et al.* 2011). Additional use of lindane on livestock, in forestry, in human pharmaceuticals and for other purposes has also been considered and is estimated to add another 150,000 t (Vijgen 2006a,b), bringing the total global figure to 600,000 t. According to Bodenstern (1972), the total HCH isomer waste was about 8 tons per ton of Lindane produced. Other experts have estimated about 10 tons per ton of Lindane produced (Krum 1982) and 10-12 tons per ton of Lindane produced (Treger 2004). Using the range of these approximations (8 to 12 tons), the total global amount of HCH waste is estimated between 4.8 and 7.2 million tons, constituting the largest international POPs stockpile.

### **10c Application Sites of PCDD/PCDF Containing Pesticides and Chemicals**

The total amount of PCDD/PCDF releases from former pesticide use and related contaminated areas has been investigated and assessed in Japan (Masunaga 2001, Seike *et al.* 2007, Weber and Masunaga 2005). Two herbicides, PCP and CNP, applied from 1950s to 1980s, contained elevated concentrations of PCDD/PCDF. In the case of CNP, the average PCDD/PCDF content in formulations produced pre-1982 was estimated to be 6 g/kg and 3.60 mg TEQ/kg active ingredient (N= 39 samples). After 1982 the PCDD/PCDF content of CNP decreased to 0.71 g/kg and 0.022 mg WHO-TEQ/kg active ingredient (N= 23 samples) (Masunaga *et al.* 2001, Seike *et al.* 2003). High PCDD/PCDF levels were found in PCP produced in the early 1960s, but also for some PCP produced at the end of the 1970s. The average dioxin content in PCP (N= 14 samples) was 3.3 g PCDD/PCDF per kilogram and 1.5 mg TEQ/kg active ingredient (Masunaga *et al.* 2001, Seike *et al.* 2003). Other pesticide formulations contained comparatively low concentrations of PCDD/PCDF (Masunaga *et al.* 2001).

The total dioxin releases from the application of pesticides on rice fields and agricultural areas in Japan during 1955-1995 was estimated based on the arithmetic average concentration of PCDD/PCDF in historical pesticides and the amount of pesticides used. The total emission from PCP use was estimated to be 540 tons of PCDD/PCDF or 250 kg TEQ. The total emission from CNP use was estimated to be 380 tons of PCDD/PCDF or 210 kg TEQ (Figure III.11.2; Weber *et al.* 2008). These loads contribute a large

proportion of today's PCDD/PCDF contamination in Japanese soil and sediments (Masunaga *et al.* 2004, Sakai *et al.* 2007). The PCDD/PCDF pattern in human milk samples from Japan has even nowadays a significant input from former PCP use (Tawara *et al.* 2006, Weber *et al.* 2008).

A historical PCDD/PCDF inventory application and PCDD/PCDF transport to rivers and ocean sediments has been established for the Tokyo Bay basin (Masunaga 2004, Weber and Masunaga 2005). For this task, the dioxin load of the Tokyo Bay basin was estimated from the annual quantities of agrochemical shipments to Tokyo, Saitama, Chiba and Kanagawa prefectures, the percentage area belonging to the basin, and the dioxin contamination of the agrochemicals. The PCDD/PCDF load of the Tokyo Bay basin due to PCP use was estimated to be approximately 31,000 kg PCDD/PCDFs and 14 kg TEQ. The contribution from CNP was estimated to be 9,300 kg PCDD/PCDF and 5 kg TEQ. The total amount of PCDD/PCDFs deposited in sediments was estimated from sediment core data (Masunaga 2004). A comparison between the total PCDD/PCDF emissions and the sediment load in Tokyo Bay shows that only a few percentages of PCDD/PCDF applied to paddy fields as agrochemical impurities have been deposited in the Tokyo Bay. Due to the persistency of these compounds, the remaining PCDD/PCDF still exist in terrestrial soil and river sediments, representing an input source into the future. According to the concentration of PCDD/PCDF in Tokyo Bay sediments, the flux from PCP use remained constant over the past 20 years. This indicates that PCDD/PCDF transport processes in the environment may last for decades and most likely centuries.

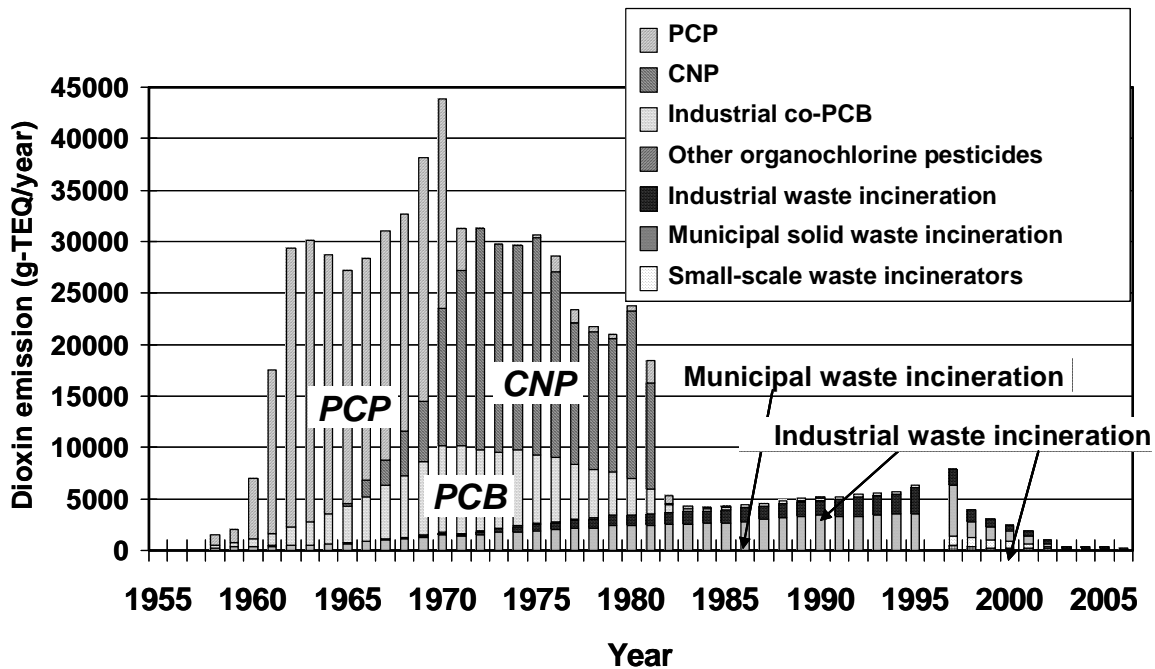


Figure III.11.2 Historic Japanese PCDD/PCDF (TEQ) release inventory to the environment

## 10f Use of PCB

### I. Inventory of PCB contaminated sites in Belarus

The inventory of PCB contaminated sites in Belarus included:

- 1) PCB-containing equipment

The first inventory of PCB-containing equipment in Belarus was developed in 2004. More than 2,000 enterprises were covered in the inventory process. The methodology is described in Kukharchyk and Kakareka (2008). About 40 companies were identified as owners of PCB-containing transformers and 750 companies as owners of PCB-containing capacitors (Government of Belarus 2006). All of these sites were treated as potential hotspots. A database was created, containing detailed information on the facilities and the PCB-containing equipment, including facility name and address, types and number of equipment, trademarks, volumes of PCB, dates of manufacture, condition of the equipment, levels of operation, descriptions of installations or storage locations. The total volume of PCB in PCB-containing equipment in Belarus was estimated at 1,500 tons. 55% of the total amount of PCB is contained in power transformers and 44% in power capacitors. A substantial part of PCB-containing equipment has been removed from service long time ago: around 25% of capacitors and 9% of transformers with a total volume of 230 tons PCB have been taken out of operation. In the past, no measures have been taken to ensure storing of PCB-containing equipment in an environmentally sound manner. The condition of power capacitors and transformers was evaluated in many cases as unsatisfactory, due to the destruction of their frames.

The sites where PCB leakages occur were also revealed. Special attention was given to open sites where the probability of PCB leakage was very high. Documented accidents were also taken into account. Special field investigations of selected sites were organized with the aim to indicate damage characteristics, features of PCB leakages, etc.

Based on the results of the investigation, PCB release factors were developed: for PCB-containing transformers – 0.3 kg/t dielectric fluid, for capacitors – 2 kg/t (EMEP/EEA 2009). It was found that approximately 1.5 tons of PCB are annually discharged into the environment from leaking power transformers and capacitors.

The potential discharges of PCDD/PCDF were calculated taking into account the total PCB leakage from PCB-containing equipment and the content of PCDD/PCDF in low chlorinated dielectrics fluids (in capacitors) and high chlorinated fluids (in transformers).

The PCB database is updated every year, including information on the total number of PCB-containing equipment and equipment taken out of service (Government of Belarus 2006).

Several projects investigating PCB-contaminated sites and soil pollution were implemented during 2005-2011 in Belarus, including on-site inspection, identification of damaged equipment, detection of leakages, soil sampling and analysis. More than 80 open sites and several dozens of closed sites where PCB-containing equipment is still in operation or in storage were investigated. As a result, the list of PCB contaminated sites was developed including facility name, address, location, type of sources, and PCB content in soil. About 60 sites were found to have polluted soil. PCB content in soil is found at levels up to milligrams or sometime grams per kilogram (Kukharchyk *et al.* 2008, 2011). The highest concentrations of PCB (up to 105 g/kg) were found in the soil near destroyed capacitors and transformers. In most cases, PCB content in soils was heterogeneous; usually there are several small hotspots within one site. The size of hotspots is different; most of them are less than 1 m<sup>2</sup>, but sometimes reach up to 50 m<sup>2</sup>. The largest polluted site has an area of more than 1000 m<sup>2</sup> and included several individual hotspots. Generally, the number of hotspots and their size depends on the area where

PCB-containing equipment is installed or stored, as well as on the quantity of PCB-containing equipment, the time of its operation or storage, the share of damaged equipment, incidents such as explosion of capacitors and PCB spraying. The highest level of pollution was found in the upper soils (top 10 cm). However, in some cases, high levels of PCB pollution were also found at depths of 1 m and more.

## 2) PCB-containing paint/varnish production

A significant source of PCB release into the environment was the use for paint and varnish production (Kukharchyk *et al.* 2008). Historical data on the annual volume of PCB in use at the Lakokraska factory in the city of Lida, Belarus were collected. It was established that during 1968-1998, about 5,000 tons of Sovol was used. The paint/varnish production process was analysed and possible ways of Sovol discharges into environment were assessed. Taking into account technological discharges of raw material, it was established that approximately 130 tons of Sovol were released into the environment (mainly in soil) on the site of the plant.

PCB content in soil was found at levels up to 96.6 mg/kg. The spatial distribution of PCB is homogenous in comparison with the places where PCB-containing equipment is installed or stored. Penta- and hexachlorobiphenyls are dominating among PCB compounds, with 53% and 28% respectively, clearly indicating that the source of PCB discharge is Sovol.

## II. Inventory of PCB contaminated sites impacting rivers and fish

The Swiss Federal Office for Environment in cooperation with the Swiss EMPA developed a methodology for inventorying PCB-impacted water bodies and classification according to the dioxin-like PCB content in fish. The inventory approach includes tracking of PCB point sources resulting in levels of dioxin-like PCB in fish above the regulation limits for fish consumption.

Monitoring data of 1,300 fish samples analysed over two decades were evaluated. For three rivers, dioxin-like toxicity levels above legislation limits were found (BAFU 2010). An inventory of impacted river sections was then established (Zennegg *et al.* 2010). Fish were contaminated within sections of 20 to 40 km of river. In a second step, river sections with elevated PCB levels in fish were screened for point sources by passive sampling.

A former disposal site (La Pila) was identified as the point source responsible for PCB contamination in the Saane river. The landfill was used for domestic and industrial waste (from 1952 to 1975). The amount of PCB was estimated to be more than 20 tons within approximately 195,000 m<sup>3</sup> waste (Zennegg 2010). Flooding events and rain washed out these PCB and enabled their migration into the river.

On the basis of PCB levels measured in fish, water bodies were classified into three categories (Zennegg 2010): the first category was defined as water bodies with PCB background contamination corresponding to levels below 4 pg WHO-TEQ/g fw (50% of the maximum level of 8 pg WHO-TEQ/g fw); the second category contains water bodies with diffuse to higher PCB load and levels of 4 to 8 pg WHO-TEQ/g fw in fish; the third category was defined as water bodies with high PCB contamination, where most fish species exceed the permitted maximum level.



## 10g Use of Chlorine for Production of Metals and Inorganic Chemicals

The pulp and paper sludge from bleaching with elemental chlorine has been highly contaminated with PCDD/PCDF and other chlorinated compounds. The application of such sludges on land or through their dumping have resulted in hotspots or contaminated land. Paper sludge residues from a German paper mill were deposited on an area of 7,000 m<sup>2</sup> during the 1970's (Rotard *et al.* 1990). The area was developed into a residential area in the 1980s. For the assessment, the area was divided into 12 sectors of about 500 to 1,000 square meters each. From each sector, 20 to 35 soil samples were taken from a depth of 0.3 m, then mixed thoroughly to give a representative sector sample. Some samples were taken at a depth of 4 meters by ram core sampling. The area was found interspersed with paper sludge lumps on the surface and at depths of 1.8 meters. Soil samples showed contamination of up to 149 ng/kg I-TEQ. The sludge lumps contained PCDD/PCDF levels between 573 to 5,165 ng/kg I-TEQ (Rotard *et al.* 1990).

## 10h Waste Incinerators

If incinerators are operated according to BAT and the wastes managed according to BEP, PCDD/PCDF contaminated sites or hotspots should not be generated except for the deposit of fly ash and air pollution control residues which can still have relatively high levels of contamination. Experience has shown that incinerators which are not well-operated and controlled can produce high levels of PCDD/PCDF emissions to all media and result in contaminated sites or hotspots.

Emissions from a chemical waste incinerator at the Coalite Chemicals plant in Bolsover (UK), which was used for the incineration of chlorinated phenol wastes, resulted in elevated PCDD/PCDF levels in cow's milk from the surrounding area (Holmes *et al.* 1994, 1998) and other foodstuff including game birds (Malisch *et al.* 1999). This case demonstrates that hazardous waste incinerators that process high proportions of products from the organochlorine industry, especially PCDD/PCDF precursors (PCB, chlorophenols, chlorobenzenes and other chlorinated aromatics), can result in high emissions of PCDD/PCDFs with considerable impacts on the local environment (Holmes *et al.* 1994, 1998). The Coalite plant also generated high levels of contamination in river sediments. Investigations by the UK National Rivers Authority found that the river sediments contained 20,269,000 ng/kg PCDD/PCDF (45,300 ng/kg TEQ) immediately downstream of the company's outfall, while the upstream levels were of only 2,030 ng/kg (9 ng/kg TEQ). The impact of the site was discernable 11 kilometres downstream on the Rother river, where sediments contained 110,000 ng/kg PCDD/PCDF (ENDS 1994).

Further, the largest release vector for PCDD/PCDF from BAT/BEP incinerators are residues and ashes from flue gas treatment, which can contaminate the environment if they are not appropriately managed. One example is the Byker municipal waste incinerator in Newcastle (UK) where ashes (generally a mixture of fly and bottom ash) were used to construct footpaths and added to the garden soils, resulting in elevated PCDD/PCDF levels in food (eggs and vegetables) (Pless-Mulloli *et al.* 2001, Watson 2001).

## 10i Recycling of e-waste



The low-tech recycling of e-waste utilizing open burning in China, India, and many other Asian and African countries has resulted in contaminated sites from these activities. Such low-tech e-waste recycling sites exist predominantly in developing and transition countries and PCDD/PCDF emissions from the open burning of PVC and partly flame retarded and PCB-containing e-waste can be very high. A wide range of PCDD/PCDF and other dioxin-like compounds including brominated and mixed halogenated dioxins, furans, biphenyls and other mixed brominated-chlorinated aromatics have been detected at open burning sites in Guiju, China (Yu *et al.* 2008, Zennegg *et al.* 2009, Leung *et al.* 2007, Li *et al.* 2007, Wong *et al.* 2007). Preliminary inventory investigations of PCDD/PCDF and dioxin-like compounds revealed contamination levels of soils above international limit values (Yu *et al.* 2008). A combination of instrumental- and bioassay-based assessments was used for adequately estimating dioxin-like toxicity. Levels up to 100 µg TEQ/kg soil have been measured at open burning sites (Yu *et al.* 2008), with brominated-chlorinated PXDD/PXDF as a main contributor (Zennegg *et al.* 2009). In the Guiyu area, where e-waste burning has been practiced for more than a decade, the contamination levels in the soils are in the kg TEQ range. These sites are also highly contaminated with heavy metals resulting in ground water pollution (Chan *et al.* 2007). All these aspects need to be considered when developing pollutant inventories for these sites.

## **10j Accidental Fires**

On December 22, 1992, a fire destroyed a warehouse containing cable drums at JSC "Irkutskcable" (Shelekhov, Irkutsk region). The fire destroyed an area of 20,000 m<sup>2</sup> around the ignition point, including adjacent warehouses containing plastic resin and paper, as well as a drying and impregnation shop. The fire lasted for 10 days, with the height of the smoke column reaching 100 m in the early stage. According to draft assessments, 600 tons of PVC plastics and 100 tons of PVC film were destroyed in the fire (Kiselev and Khudolej 1997). For technical reasons, fire masks were not used. Acute poisoning has been confirmed for 69 firefighters; 43 of them were recognized as disabled. As a result of incomplete combustion, PCDD/PCDF were released. The soot formed during the decomposition of PVC cables contained up to 200 ng PCDD/PCDF per gram. It should be noted, however, that the uncertainty of the results is high due to the limited volume of samples analyzed.

## **10k Dredging of Sediments and Contaminated Flood Plains**

The Elbe river has been impacted during almost a century by POPs (PCDD/PCDF, HCHs, DDT etc.) and other pollutants such as Organo-tin from industrial discharges, including organochlorine production and other industries using chlorine in the Bitterfeld region of Germany. The sediments and floodplains were shown to be contaminated with PCDD/PCDF approximately 350 km downstream - as far as Hamburg and even the North Sea (Götz *et al.* 2007). The sources of pollution have been assessed and an inventory developed, showing that approximately 60 km<sup>2</sup> of lowland area downstream of the Spittelwasser creek are heavily contaminated by PCDD/PCDF, HCH and DDT. The pollutant reservoir includes 20,000 m<sup>3</sup> of highly contaminated PCDD/PCDF sediments (Förstner and Salomonis 2010). PCDD/PCDF levels in the floodplains soils reached up to 2,100 ng I-TEQ/kg. In addition to inventory activities, the options for the different zones along the river (river shore, inner dyke, outer dyke) have been assessed taking into account the EU food limits for managing cattle and feedstuff in the floodplains (Schulz *et al.* 2005, Kamphues *et al.* 2011). While milk from grazing cows and meat from permanent grazing animals is

above the EU food limits and can not be produced, certain techniques have been developed for harvesting the grass/hay so that it can be used for feeding. Recommendations for farmers using contaminated grassland for feed and food production were developed (Kamphues *et al.* 2011)) and can be regarded as a pilot case for inventory and managing other floodplains contaminated with PCDD/PCDF or PCB and the related pollutant reservoirs upstream (Förstner and Salomon 2010).

## **101 Dumps of Wastes/Residues from Source Groups 1-9**

### **Teshima Island (Japan)**

More than 500,000 tons of mixed industrial wastes were illegally dumped into a 30 ha gravel pit site on Teshima Island in Japan from 1970 until 1988 (Takeda 2007). Major components included shredder residues from end-of-life vehicles and electric appliances, paper mill sludges, slags, dewatered industrial sludge, incineration residues. A detailed assessment and inventory of the wastes, surrounding soil, groundwater and surface water was conducted. It revealed that wastes and soil were contaminated with notable quantities of heavy metals and chlorinated organic compounds, including an estimated 1.5 kg TEQ PCDD/PCDF (Takeda 2007). Water soluble pollutants contaminated groundwater with a risk of releases to the sea and shore. A remediation plan was established to excavate the waste and the contaminated soil and transport this material to a neighbouring island where an incinerator and a melting plant was built (Takeda 2007). The cost of the remediation work was estimated at 428 million US\$, while the operation of the dumpsite had generated approximately 3 million US\$ revenue (Takeda 2007).

### **Love Canal (United States)**

The example at the Love Canal site in the Niagara County also shows successful site remediation and cleanup procedure.<sup>35</sup> The site encompasses a hazardous waste landfill where chemical waste products were disposed of from 1942 to 1952 by an Electrochemical Company. It first came into national prominence in the late 1970s, when it was discovered that contaminated leachate had migrated to the surface of the canal and to nearby residential basements. Contaminants also migrated to nearby creeks via the sewage system. Scientific studies did not conclusively prove that these chemicals were responsible for residents' illnesses, and scientists were divided on the issue, even though eleven known or suspected carcinogens had been identified, one of the most prevalent being benzene. Polychlorinated dibenzodioxins were also found, with levels measured in water samples of 53 ppb.

In October 1978, containment measures were undertaken, including the construction of a tile drain and leachate collection system, placement of a clay cap over 16 acres of the canal, creation of an on-site leachate treatment facility and installation of a fence around the area. Approximately 1,000 families have been relocated from the area.

In 1984, 40 acres were covered by a synthetic liner and clay cap and surrounded by a barrier drainage system. A long-term monitoring study was implemented to evaluate the effectiveness of the leachate collection system and assess the contaminant migration in soil and groundwater. In September 2004, the EPA removed the Love Canal site from the National Priorities List (NPL). All cleanup work had been

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<sup>35</sup> <http://www.epa.gov/history/topics/lovecanal/index.html>

completed, and follow-up monitoring conducted over the past 15 years confirms that the cleanup goals have been reached. The site will continue to be monitored and remains eligible for cleanup work in the event that a change in site conditions should warrant such an action.

The discovery of toxic waste dumps such as the Love Canal led to the adoption of the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) in the United States. CERCLA is commonly referred to as the "Superfund" because of the fund established to help the cleanup in residential locations (<http://www.epa.gov/superfund/>). The Superfund cleanup process involves steps to assess sites, placing them on the National Priorities List (NPL), and establish and implement appropriate cleanup plans. Over the past years, tens of thousands of hazardous waste sites and other polluted sites were located and analyzed. Currently, 13,742 sites are listed, among which 1,723 sites belong to the NPL. The inventory contains 225 sites polluted by PCDD/PCDF, among which 210 NPL sites, and 488 sites polluted by PCB, including 431 NPL sites.

## **10m Kaolin or Ball Clay Sites**

Several kaolin and ball clay deposits have been found to be contaminated with PCDD/PCDF in different regions in the world (Hori *et al.* 2011). The Dutch governmental institute RIKILT analysed 28 samples of "pregnancy clays" (20 from Africa and 8 bought in The Netherlands) for the presence of PCDD/PCDF as part of a first inventory of contaminated clays in some African countries (Uganda, Kenya, Tanzania, Nigeria, Mali, Ivory Coast and Zimbabwe). In some regions, such as Africa and South America, clay minerals and soils are consumed by pregnant women as a cure for morning sickness and possibly a source of minerals such as iron. Clay for this use is available for sale in many parts of the world. Consumption can be as high as 300 gram per day, but average daily intake seems to be around 30-80 gram (Hoogenboom *et al.* 2011). The study assessed whether the clays were contaminated and carried a potential risk for the newborns. Four of these samples showed relatively high levels of PCDD/PCDF: 66 ng TEQ/kg product (Mabele, Cameroon), 66 ng TEQ/kg product (Mabele, Democratic Republic of Congo), 75 ng TEQ/kg product (Kaolin, Côte d'Ivoire) and 103 ng TEQ/kg product (Mabele, country of origin unknown). In addition, a sample from Nigeria (Nzu) had a level of 24 ng TEQ/kg product and a sample from Cameroon (Mabele) had a level of 4.5 ng TEQ/kg product. Levels in other samples were much lower (Hoogenboom *et al.* 2011). Only PCDDs contributed to these TEQ levels, but the congener patterns were not the same for all clay samples.

The WHO/UNEP coordinated study on human milk included a number of African countries. The clay data have been compared with human milk data to evaluate whether the consumption of clay may add to the dioxin exposure. The highest PCDD/PCDF levels in African samples were observed in Côte d'Ivoire (11.1 pg TEQ/g fat) and the Democratic Republic of Congo (11.1 pg TEQ/g fat) whilst the other samples were in the range of 1.5 to 3.9 pg TEQ/g fat (Malisch *et al.* 2011). The PCDD/PCDF pattern of the clay and human milk samples, along with the relatively high levels measured in Congo and the Ivory Coast suggest that the use of clay during pregnancy contributes to these high PCDD/PCDF levels in human milk. Due to vulnerability to PCDD/PCDF in the fetal development phase and for the newborn, the use of contaminated clays should be prevented. Inventories of clays used for human consumption or as animal feed additive should be carried out as a matter of urgency.

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