# 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-$Cl_4$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-subsituted 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 | $WHO_{1998}$-TEF | $WHO_{2005}$-TEF |
|---|---|---|---|
| Polychlorinated dibenzo-*p*-dioxins | | | |
| 2378-$Cl_4$DD | 1 | 1 | 1 |
| 12378-$Cl_5$DD | 0.5 | 1 | 1 |
| 123478-$Cl_6$DD | 0.1 | 0.1 | 0.1 |
| 123678-$Cl_6$DD | 0.1 | 0.1 | 0.1 |
| 123789-$Cl_6$DD | 0.1 | 0.1 | 0.1 |
| 1234678-$Cl_7$DD | 0.01 | 0.01 | 0.01 |
| $Cl_8$DD | 0.001 | 0.0001 | 0.0003 |
| Polychlorinated dibenzofurans | | | |
| 2378-$Cl_4$DF | 0.1 | 0.1 | 0.1 |
| 12378-$Cl_5$DF | 0.05 | 0.05 | 0.03 |
| 23478-$Cl_5$DF | 0.5 | 0.5 | 0.3 |
| 123478-$Cl_6$DF | 0.1 | 0.1 | 0.1 |
| 123678-$Cl_6$DF | 0.1 | 0.1 | 0.1 |
| 123789-$Cl_6$DF | 0.1 | 0.1 | 0.1 |
| 234678-$Cl_6$DF | 0.1 | 0.1 | 0.1 |
| 1234678-$Cl_7$DF | 0.01 | 0.01 | 0.01 |
| 1234789-$Cl_7$DF | 0.01 | 0.01 | 0.01 |
| $Cl_8$DF | 0.001 | 0.0001 | 0.0003 |
| Non-*ortho* 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-*ortho* 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-$Cl_4$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 substantialcontributions 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).

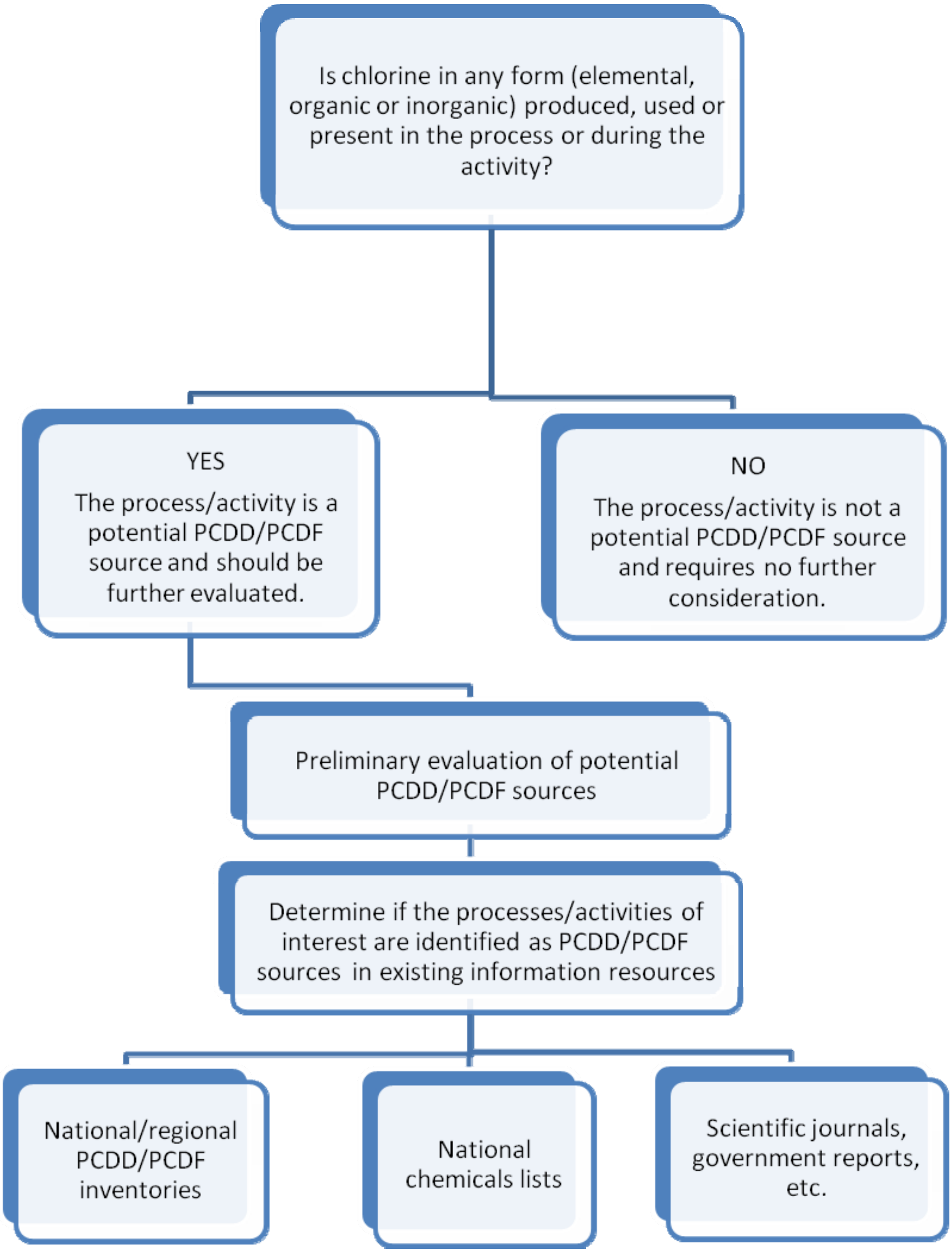

**Figure III.2.1 Simple screening matrix for identifying PCDD/PCDF sources**

**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 *et al.* 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 *et al*. 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 ($AlCl_3$), cuprous chloride ($CuCl_2$) cupric chloride ($CuCl_3$), and ferric chloride ($FeCl_3$) 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 $FeCl_3$ (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 *et al*. (2009) |

| | |
|---|---|
| | derived an $EF_{WATER}$ of 5.667 ng TEQ/t for this process, and Jin *et al*.(2009) derived an $EF_{RESIDUE}$ of 126.69 µg TEQ/t. 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 *et al*. 2009) and to the use of a chlorine-based oxidizing agent for purifying the crude acetylene (Kawamoto 2002). |
| Trichloroethylene (CAS 79-01-6) | PCDD/PCDF were reported at a concentration of 0.7 ng TEQ/kg in trichloroethylene made by Solvay in France (van Hattam *et al*. 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. |
| Epichlorohydrin (1-Chloro-2,3-epoxypropane, CAS 106-89-8 ) | 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 *et al*. 1994). PCDD/PCDF have been reported in epichlorohdrin itself and in process wastewater from its production (Fiedler 1994, Lee *et al.* 2009). Lee *et al*. (2009) measured PCDD/PCDF in wastewater from an epichlorohydrin production facility in Taiwan and derived an $EF_{WATER}$ of 5.8 ng TEQ/t. Also a PCDD/PCDF concentration of 1.82 ng TEQ/kg in epichlorohydrin was reported by Fiedler (1994). |
| Chloroprene(2-chloro-1,3-butadiene, CAS 126-99-8) and Polychloroprene (Neoprene, CAS 9010-98-4) (Polymer of 2-chloro-1,3-butadiene) | PCDD/PCDF were detected at a concentration of 90 ng TEQ/kg in polychloroprene (Neoprene) produced by a Dutch manufacturer (van Hattum *et al*. 2004). PCDD/PCDF also occurred at 209 pg TEQ/$m^3$ in vent gases from the same facility, which produced epichlorohydrin, allyl chloride and PVC. |
| Hexachlorocyclohexane (CAS 608-73-1) | PCDD/PCDF were reported in hexachlorocyclohexane (Zheng *et al*. 2008). |
| Tetrachlorobenzene (CAS 95-94-3) | 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). |
| Chlorinated PVC (C-PVC, CAS 9002-86-2) | PDCC/PCDF as high as 32,000 ng TEQ/kg have been detected in C-PVC (van der Weiden and van der Kolk 2000). |
| Aromatic polyamides (Aramids) and precursors | PCDD/PCDF were reported at a concentration of 0.137 ng I-TEQ/$m^3$ in process vent gas (van Hattum et al. 2004) and have also been detected in wastewater (van der Weiden and van der Kolk 2000). |
| Chlorinated methanes (methylene chloride, chloroform and carbon | Data submitted to the U.S. Environmental Protection Agency show detectable levels of PCDD/PCDF are released in wastewater (Weiss 2006). |

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|---|---|
| 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<br>(2*RS*)-2-(2,4-dichlorophenoxy)propionic acid (CAS 120-36-5) | 35,000 | Hansen (2000) |
| Nitrophen (NIP) =<br>2,4-dichlorophenyl-4'-nitrophenyl ether (CAS 1836-75-5) | 1,500 | Masunaga (1999) |
| Lindane (γ -hexachlorocyclohexane, γ-HCH)<br>1α,2α,3β,4α,5α,6β-hexachlorocyclohexane (CAS 58-89-9) | 216[a]<br>(2.1-430 range) | Holt et al. (2010) |
| Chlorothalonil<br>2,4,5,6-tetrachloroisophthalonitrile (CAS 1897-45-6) | 110[b] | Holt et al. (2010) |
| | 240 | Masunaga (1999) |
| Dicofol<br>2,2,2-trichloro-1,1-bis(4-chlorophenyl)ethanol (CAS 115-32-2) | 84 | Li et al. (2009) |
| Chlorthal<br>tetrachloroterephthalic acid (CAS 2136-79-0) | 58.5[a]<br>(57-60 range) | Holt et al. (2010) |
| MCPA/Dicamba<br>2-Methyl-4-chlorophenoxyacetic acid (CAS 94-74-6)<br>3,6-Dichloro-2-methoxybenzoic acid (CAS1918-00-9) | 48.3[a]<br>(0.69-96 range) | Holt et al. (2010) |
| Tiller<br>• CPA-2EH ester, 32.1%<br>(*RS*)-2-ethylhexyl 4-chloro-*o*-tolyloxyacetate (CAS 29450-45-1)<br>• 2,4-D isooctylester, 10.4%<br>iso-octyl (2,4-dichlorophenoxy)acetate (CAS 25168-26-7)<br>• Fenoxaprop-p-ethyl, 4.4%<br>ethyl (*R*)-2-[4-(6-chloro-1,3-benzoxazol-2-yloxy)phenoxy]propionate (CAS 71283-80-2) | 19.8[c] | Huwe et al. (2003) |

| | | |
|---|---|---|
| Fluroxypyr<br>4-Amino-3,5-dichloro-6-fluoro-2-pyridyloxyacetic acid (CAS 69377-81-7) | 17[b] | Holt et al. (2010) |
| 2,4-DB<br>4-(2,4-dichlorophenoxy)butyric acid<br>(CAS 94-82-6) | 8.8[a]<br>(7.5-10 range) | Holt et al. (2010) |
| Assure II = Quizalofop P-Ethyl<br>ethyl (2*R*)-2-[4-(6-chloroquinoxalin-2-yloxy)phenoxy]propionate (CAS 100646-51-3) | 4.1 | Huwe et al. (2003) |
| Imazamox<br>2-[(*RS*)-4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl]-5-methoxymethylnicotinic acid (CAS 114311-32-9) | 3.1[a]<br>(1.3-4.9 range) | Holt et al. (2010) |
| Flumetsulam<br>2',6'-difluoro-5-methyl[1,2,4]triazolo[1,5-a]pyrimidine-2-sulfonanilide (CAS 98967-40-9) | 2.9[a]<br>(2.4-3.4 range) | Holt et al. (2010) |
| MCPA<br>2-methyl-4-chlorophenoxyacetic acid (CAS 94-74-6) | 2.8[b] | Holt et al. (2010) |
| | 2,000 | Masunaga (1999) |
| Triclopyr/picloram<br>3,5,6-Trichloro-2-pyridinyloxyacetic acid (CAS 55335-06-3)<br>4-Amino-3,5,6-trichloro-2-pyridinecarboxylic acid (CAS 1918-02-1) | 2.5[b] | Holt et al. (2010) |
| Mecoprop/Dicamba =<br>(RS)-2-(4-chloro-2-methylphenoxy)propanoic acid (CAS 93-65-2 and CAS 7085-19-0)<br>3,6-Dichloro-2-methoxybenzoic acid (CAS 1918-00-9) | 0.068[b] | Holt et al. (2010) |
| Fenamiphos<br>(*RS*)-(ethyl 4-methylthio-*m*-tolyl isopropylphosphoramidate) (CAS 22224-92-6) | 0.058[b] | Holt et al. (2010) |

[a] Mean of two lower bound values.

[b] Lower bound values

[c] ng TEQ/g of ready-for-use product (active ingredient plus adjuvants).

[d] 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/$m^3$ for a rotary furnace, afterburner and sleeve filters; 0.41 ng TEQ/$m^3$ for a |

| | |
|---|---|
| | static furnace, afterburner and sleeve filters; 21 ng TEQ/$m^3$ for a static furnace, afterburner without carbon system; 0.55 ng TEQ/$m^3$ for combustion chamber, afterburner and sleeve filters; 0.026 ng TEQ/$m^3$ combustion chamber, afterburner, sleeve filters, and lime + carbon abatement process (Baldassini *et al*. 2009). |
| Heat treatment of food salt | PCDD/PCDF have been detected at considerably higher levels in processed food salt than in natural salt. Comparing bamboo-salt and parched salt, Yang *et al*. (2004) found PCDD/PCDF levels were generally very low, with bamboo-salt having highest levels – from 5.7 x $10^{-5}$–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 *et al*. 2002). |

# 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[19]. 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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[19] 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**

# National Inventory of Unintentional Releases of Persistent Organic Pollutants under the Stockholm Convention

## Reference Year 20___ (January 1-December 31)

| | |
|---|---|
| **Requested by:** | [Institution’s name with street address;<br>contact person with phone and fax number; e-mail address] |
| **To:** | [Institution’s name with street address and other coordinates] |
| Purpose and context: | [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 unintentionaly 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. |
| **Please return the completed questionnaire to the above sender not later than** | ______________________ (Date) |

**Questionnaire 1: Group 1 - Waste Incineration**

| | | |
|---|---|---|
| Type of Plant | Municipal solid waste<br>Industrial waste<br>Hospital waste<br>Light shredder<br>Sewage sludge<br>Waste wood and waste biomass<br>Animal carcasses | [ ]<br>[ ]<br>[ ]<br>[ ]<br>[ ]<br>[ ]<br>[ ] |
| Name of Plant | | |
| Location (City/Province) | | |
| Address | | |
| Contact<br>(Name, position, phone and fax numbers, e-mail) | | |
| Number of Furnaces | | |
| Type of Operation | Batch (*e.g.*, 100 kg per batch)<br>Semi-continuous (*e.g.*, 8 hours per day)<br>Continuous (24 hours per day) | [ ]<br>[ ]<br>[ ] |
| Annual Operational/Capacity (per Unit) | t/h (tons per hour)<br>h/d (hours per day)<br>d/w (days per week)<br>t/d (tons per day)<br>d/a (days per year)<br>h/a (hours per year)<br>t/a (tons per year) | |
| Annual Operation/Capacity (total) | t/h (tons per hour)<br>h/d (hours per day)<br>d/w (days per week)<br>t/d (tons per day)<br>d/a (days per year)<br>h/a (hours per year)<br>t/a (tons per year) | |
| Type of Furnace | Mass burn waterwall (grate)<br>Fluidized bed<br>Stoker<br>Rotary kiln<br>Other (please specify) | |
| Temperature in Furnace | Main furnace (°C)<br>Afterburner/second chamber (°C) | |
| Type of Air Pollution Control System (APCS) | Electrostatic precipitator<br>Cyclone | [ ]<br>[ ] |

| | | | |
|---|---|---|---|
| | Bag filter<br>Wet scrubber<br>Dry scrubber<br>Lime injection<br>NaOH/alkali injection<br>Active carbon/coke injection<br>Active carbon filter<br>Catalytic converter (SCR)<br>Induced or forced draft fan<br>Other (please specify)<br>None | | [ ]<br>[ ]<br>[ ]<br>[ ]<br>[ ]<br>[ ]<br>[ ]<br>[ ]<br>[ ]<br><br>[ ] |
| Heat Recovery System | Yes [ ] | No [ ] | |
| Temperature of Gases | At entry to APCS (°C) [ ] | At exit from APCS (°C) [ ] | |
| Flux of Exit Gases | ($m^3$/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)

| | **Emission Factor (µg TEQ/t)** | | | | |
|---|---|---|---|---|---|
| **Class** | **Air** | **Water** | **Land** | **Product** | **Residues** |
| | | | | | |
| | **Annual Release (g TEQ/a)** | | | | |
| **Annual Activity (t/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<br>(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)<br>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 | ($m^3$/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)

| | **Emission Factor (µg TEQ/t)** | | | | |
|---|---|---|---|---|---|
| **Class** | **Air** | **Water** | **Land** | **Product** | **Residues** |
| | | | | | |
| | **Annual Release (g TEQ/a)** | | | | |
| **Annual Activity (t/a)** | **Air** | **Water** | **Land** | **Product** | **Residues** |

**Questionnaire 3: Group 3 – Power Generation and Heating**

| | | |
|---|---|---|
| Type of Plant | **Power plants** | |
| | Coal | [ ] |
| | Lignite | [ ] |
| | Bituminous coal | [ ] |
| | Anthracite | [ ] |
| | Other | |
| | Natural gas | [ ] |
| | Wood | [ ] |
| | Landfill gas | [ ] |
| | Sewer gas | [ ] |
| | Biomass (please specify) | |
| | **Industrial Combustion units (small)** | |
| | 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)<br>TJ/a (Terajoule per year) | |
| Type of Furnace/Combustor | Boiler<br>Process heater<br>Flare<br>Turbine (internal gas)<br>Combustion engine (internal)<br>Other (please specify) | |
| Temperature in Furnace | Main furnace (°C)<br>Second chamber/afterburner (°C) | |
| Type of Abatement Pollution Control System (APCS) | Electrostatic precipitator<br>Cyclone<br>Bughouse filter<br>Wet scrubber<br>Dry scrubber<br>Lime injection<br>NaOH/alkali injection<br>Active carbon/coke injection<br>Active carbon filter<br>Catalytic converter (SCR)<br>Other (please specify)<br>None | [ ]<br>[ ]<br>[ ]<br>[ ]<br>[ ]<br>[ ]<br>[ ]<br>[ ]<br>[ ]<br>[ ]<br><br>[ ] |
| Heat Recovery System | Yes [ ] | No [ ] |
| Temperature of Gases | At entry to APCS (°C) [ ] | At exit from APCS (°C) [ ] |
| Flux of Exit Gases | ($m^3$/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)

| | **Emission Factor (µg TEQ/t)** | | | | |
|---|---|---|---|---|---|
| **Class** | **Air** | **Water** | **Land** | **Product** | **Residues** |
| | | | | | |
| | **Annual Release (g TEQ/a)** | | | | |
| **Annual Activity (t/a)** | **Air** | **Water** | **Land** | **Product** | **Residues** |
| | | | | | |

## Questionnaire 4: Group 4 – Mineral Production

| | | |
|---|---|---|
| Type of Plant | Cement | [ ] |
| | Lime | [ ] |
| | Brick | [ ] |
| | Glass | [ ] |
| | Ceramics | [ ] |
| | Asphalt mixing | [ ] |
| Address | | |
| Contact<br>(Name, position, phone and fax numbers, e-mail) | | |
| Number of Furnaces | | |
| Feed Materials<br>(type, quantity = t/a) | | |
| Primary Fuel<br>(type, quantity = t/a) | | |
| Secondary/Alternative Fuel<br>(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) | |
| | 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 | Rotary kiln | |
| | Shaft kiln | |
| | Tunnel furnace | |

| | | |
|---|---|---|
| | Other (please specify) | |
| Temperature in Furnace | Main furnace (°C)<br>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 | ($m^3$/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)

| | **Emission Factor (µg TEQ/t)** | | | | |
|---|---|---|---|---|---|
| **Class** | **Air** | **Water** | **Land** | **Product** | **Residues** |
| | | | | | |
| | **Annual Release (g TEQ/a)** | | | | |
| **Annual Activity (t/a)** | **Air** | **Water** | **Land** | **Product** | **Residues** |
| | | | | | |

**Questionnaire 5: Group 5 – Transport**

| | | | |
|---|---|---|---|
| Region/Province/Nation. | | | |
| Address | | | |
| Contact<br>(Name, position, phone and fax numbers, e-mail) | | | |
| **Type of fuel** | **Leaded Gasoline** | **Unleaded Gasoline** | **Diesel/Light Fuel Oil** |
| Annual national fuel consumption in liter per year (L/a) | | | |
| **Passenger Cars** | | | |
| 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) | | | |
| **Busses** | | | |
| 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) | | | |
| **Busses and Trucks** | | | |
| 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) | | | |
| **Ships** | | | |
| 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) | | | |
| **Trains** | | | |
| 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)

| | **Emission Factor (μg TEQ/t)** | | | | |
|---|---|---|---|---|---|
| **Class** | **Air** | **Water** | **Land** | **Product** | **Residues** |
| | | | | | |
| | **Annual Release (g TEQ/a)** | | | | |
| **Annual Activity (t/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<br>(Name, position, phone and fax numbers, e-mail) | |

| **Biomass burning** | | | |
|---|---|---|---|
| Type of biomass, *e.g.,* pine, sugarcane, *etc.* | 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 | | | |

| **Open Waste Burning and Accidental Fires** | | | | | | |
|---|---|---|---|---|---|---|
| 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)

| | **Emission Factor (µg TEQ/t)** | | | | |
|---|---|---|---|---|---|
| **Class** | **Air** | **Water** | **Land** | **Product** | **Residues** |
| | | | | | |
| | **Annual Release (g TEQ/a)** | | | | |
| **Annual Activity (t/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:<br>Type of Plant | Pulp and paper industry: Pulp<br>Pulp and paper industry: Paper (primary or recycling)<br>Pulp and paper - integrated<br>Organochlorine production<br>Ethylene dichloride<br>PVC<br>Pesticides (PCP, 2,4,5-T, 2,4-D)<br>Production of chlorine gas (graphite electrodes)<br>Petroleum industry refineries | [ ]<br>[ ]<br>[ ]<br><br>[ ]<br>[ ]<br>[ ]<br>[ ]<br>[ ] |
| Address | | |
| Contact<br>(Name, position, phone and fax numbers, e-mail) | | |
| Capacity: Consumption of Raw Materials<br>(type, quantity = t/a) | | |
| Capacity: Final Product of Raw Materials<br>(type, quantity = t/a) | | |
| Type of Process | Fixed-bed<br>Fluidized bed<br>Other | [ ]<br>[ ]<br>[ ] |
| Type of Operation | Batch (*e.g.*, 100 kg per batch)<br>Semi-continuous (*e.g.*, 8 hours per day)<br>Continuous (24 hours per day) | [ ]<br>[ ]<br>[ ] |
| Annual Operation/Capacity (per Unit) | t/h (tons per hour)<br>h/d (hours per day)<br>d/w (days per week)<br>t/d (tons per day)<br>d/a (days per year)<br>h/a (hours per year)<br>t/a (tons per year) | |
| Annual Operation/Capacity (total) | t/h (tons per hour)<br>h/d (hours per day)<br>d/w (days per week)<br>t/d (tons per day)<br>d/a (days per year)<br>h/a (hours per year)<br>t/a (tons per year) | |

| | | |
|---|---|---|
| Operation/Production Temperature | (°C) | |
| Water discharge (L/h, $m^3$/a) | | |
| Water treatment | Settling pond<br>Aerated lagoon<br>Secondary treatment<br>Tertiary Treatment<br>Others (please specify) | [ ]<br>[ ]<br>[ ]<br>[ ]<br>[ ] |
| Sludge generation | t/a (tons per year) | |
| Sludge disposal | Landfill (t/a)<br>Land farming (t/a)<br>On-site (t/a)<br>Incineration (t/a)<br>Others (please specify) (t/a) | |
| Type of Air Pollution Control System (APCS) | Electrostatic precipitator<br>Cyclone<br>Bag filter<br>Wet scrubber<br>Dry scrubber<br>Lime injection<br>NaOH/alkali injection<br>Active carbon/coke injection<br>Active carbon filter<br>Catalytic converter (SCR)<br>Induced or forced draft fan<br>Other (please specify)<br>None | [ ]<br>[ ]<br>[ ]<br>[ ]<br>[ ]<br>[ ]<br>[ ]<br>[ ]<br>[ ]<br>[ ]<br>[ ]<br><br>[ ] |
| Temperature of Gases | At entry to APCS (°C) [ ] | At exit from APCS (°C) [ ] |
| Flux of Exit Gases | ($m^3$/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)

| | **Emission Factor (µg TEQ/t)** | | | | |
|---|---|---|---|---|---|
| **Class** | **Air** | **Water** | **Land** | **Product** | **Residues** |
| | | | | | |
| | **Annual Release (g TEQ/a)** | | | | |
| **Annual Activity (t/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 µg 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) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Residue | |
| | | | | Air | Water | Land | Product | Fly Ash | Bottom Ash |
| 1 | | | **Waste incineration** | | | | | | |
| | a | | **Municipal solid waste incineration** | | | | | | |
| | | 1 | Low technol. combustion, no APCS | 3,500 | | NA | NA | ND | 75 |
| | | | *LoC* | *M* | | | | | *M* |
| | | 2 | Controlled comb., minimal APCS | 350 | | NA | NA | 500 | 15 |
| | | | *LoC* | *M* | | | | *M* | *M* |
| | | 3 | Controlled comb., good APCS | 30 | | NA | NA | 200 | 7 |
| | | | *LoC* | *M* | | | | | *M* |
| | | 4 | High tech. combustion, sophisticated APCS | 0.5 | | NA | NA | 15 | 1.5 |
| | | | *LoC* | *M* | | | | *M* | *M* |
| | b | | **Hazardous waste incineration** | | | | | | |
| | | 1 | Low technol. combustion, no APCS | 35,000 | | NA | NA | 9,000 | |
| | | | *LoC* | *L* | | | | *L* | |
| | | 2 | Controlled comb., minimal APCS | 350 | | NA | NA | 900 | |
| | | | *LoC* | *L* | | | | *L* | |
| | | 3 | Controlled comb., good APCS | 10 | | NA | NA | 450 | |
| | | | *LoC* | *L* | | | | *L* | |
| | | 4 | High tech. combustion, sophisticated APCS | 0.75 | | NA | NA | 30 | |
| | | | *LoC* | *L* | | | | *L* | |
| | c | | **Medical waste incineration** | | | | | | |
| | | 1 | Uncontrolled batch combustion, no APCS | 40,000 | | NA | NA | | 200 |
| | | | *LoC* | *L* | | | | | *L* |
| | | 2 | Controlled, batch, no or minimal APCS | 3,000 | | NA | NA | | 20 |
| | | | *LoC* | *L* | | | | | *L* |
| | | 3 | Controlled, batch comb., good APCS | 525 | | NA | NA | 920 | |
| | | | *LoC* | *M* | | | | *M* | |
| | | 4 | High tech, continuous, sophisticated APCS | 1 | | NA | NA | 150 | |
| | | | *LoC* | *M* | | | | *M* | |
| | d | | **Light fraction shredder waste incineration** | | | | | | |
| | | 1 | Uncontrolled batch comb., no APCS | 1,000 | | NA | NA | ND | |
| | | | *LoC* | *L* | | | | | |
| | | 2 | Controlled, batch, no or minimal APCS | 50 | | NA | NA | ND | |
| | | | *LoC* | *M* | | | | | |
| | | 3 | High tech, continuous, sophisticated APCS | 1 | | NA | NA | 150 | |
| | | | *LoC* | *M* | | | | *M* | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | **e** | | **Sewage sludge incineration** | | | | | | |
| | | 1 | Old furnaces, batch, no/little APCS | 50 | | NA | NA | 23 | |
| | | | *LoC* | *M* | | | | *M* | |
| | | 2 | Updated, continuously, some APCS | 4 | | NA | NA | 0.5 | |
| | | | *LoC* | *M* | | | | *M* | |
| | | 3 | State-of-the-art, full APCS | 0.4 | | NA | NA | 0.5 | |
| | | | *LoC* | *M* | | | | *M* | |
| | **f** | | **Waste wood and waste biomass incineration** | | | | | | |
| | | 1 | Old furnaces, batch, no/little APCS | 100 | | NA | NA | 1,000 | |
| | | | *LoC* | *M* | | | | *M* | |
| | | 2 | Updated, continuously, some APCS | 10 | | NA | NA | 10 | |
| | | | *LoC* | *M* | | | | *M* | |
| | | 3 | State-of-the-art, full APCS | 1 | | NA | NA | 0.2 | |
| | | | *LoC* | *M* | | | | *M* | |
| | **g** | | **Animal carcasses burning** | | | | | | |
| | | 1 | Old furnaces, batch, no/little APCS | 500 | | NA | NA | | ND |
| | | | *LoC* | *M* | | | | | |
| | | 2 | Updated, continuously, some APCS | 50 | | NA | NA | | ND |
| | | | *LoC* | *M* | | | | | |
| | | 3 | State-of-the-art, full APCS | 5 | | NA | NA | | ND |
| | | | *LoC* | *M* | | | | | |

**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 | | | **Ferrous and Non-Ferrous Metal Production** | | | | | |
| | a | | **Iron ore sintering** | | | | | |
| | | 1 | 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 | | **Coke production** | | | | | |
| | | 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 | | **Iron and steel production plants and foundries** | | | | | |
| | | | **Iron and steel plants** | | | | | |
| | | 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* | | | | |
| | | | **Foundries** | | | | | |
| | | 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 scribber | 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* |
| | | | **Hot-dip galvanizing plants** | | | | | |
| | | 1 | Facilities without APCS | 0.06 | NA | NA | NA | 0.01 |
| | | | *LoC* | *M* | | | | *L* |
| | | 2 | Facilties 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* |
| | d | | **Copper production** | | | | | |
| | | 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* | | | |
| | e | | **Aluminum production** | | | | | |
| | | 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 |
| | f | | **Lead production** | | | | | |
| | | 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* | | | | |
| | g | | **Zinc production** | | | | | |
| | | 1 | Kiln with no dust control | 1,000 | ND | NA | NA | 0.02 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | *LoC* | *M* | | | | *M* |
| | | 2 | Hot briquetting/rotarry 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* | | | | |
| | h | | **Brass and bronze production** | | | | | |
| | | 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* | | | | |
| | i | | **Magnesium production** | | | | | |
| | | 1 | Using MgO/C thermal treatment in Cl2, no effluent treatment, poor APCS | 250 | 9,000 | NA | NA | 0 |
| | | | *LoC* | *M* | *M* | | | |
| | | 2 | Using MgO/C thermal treatment in Cl2, comprehensive pollution control | 50 | 30 | NA | NA | 9,000 |
| | | | *LoC* | *H* | *H* | | | *M* |
| | | 3 | Thermal reduction process | 3 | ND | NA | NA | NA |
| | | | *LoC* | *H* | | | | |
| | j | | **Thermal Non-ferrous metal production (*e.g.*, Ni)** | | | | | |
| | | 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* | | | | |
| | k | | **Shredders** | | | | | |
| | | 1 | Metal shredding plants | 0.2 | NA | NA | ND | 5 |
| | | | *LoC* | *H* | | | | *H* |
| | l | | **Thermal wire reclamation and e-waste recycling** | | | | | |
| | | 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 |
| **3** | | | **Heat and Power Generation** | | | | | |
| | **a** | | **Fossil fuel power plants** | | | | | |
| | | 1 | Fossil fuel/waste co-fired power boilers<br>*LoC* | 35<br>*L* | ND | NA | NA | ND |
| | | 2 | Coal fired power boilers<br>*LoC* | 10<br>*M* | ND | NA | NA | 14<br>*H* |
| | | 3 | Peat fired power boilers<br>*LoC* | 17.5<br>*L* | ND | NA | NA | ND |
| | | 4 | Heavy fuel fired power boilers<br>*LoC* | 2.5<br>*M* | ND | NA | NA | ND |
| | | 5 | Shale oil fired power plants<br>*LoC* | 1.5<br>*L* | ND | NA | NA | ND |
| | | 6 | Light fuel oil/natural gas fired power boilers<br>*LoC* | 0.5<br>*H* | ND | NA | NA | ND |
| | **b** | | **Biomass power plants** | | | | | |
| | | 1 | Mixed biomass fired power boilers<br>*LoC* | 500<br>*M* | ND | NA | NA | ND |
| | | 2 | Clean wood fired power boilers<br>*LoC* | 50<br>*H* | ND | NA | NA | 15<br>*H* |
| | | 3 | Straw fired boilers<br>*LoC* | 50<br>*M* | ND | NA | NA | 70<br>*M* |
| | | 4 | Boilers fired with bagasse, rice husk etc.<br>*LoC* | 50<br>*L* | ND | NA | NA | 50<br>*L* |
| | **c** | | **Landfill biogas combustion** | | | | | |
| | | 1 | Biogas-/landfill gas fired boilers, motors/turbines and flaring<br>*LoC* | 8<br>*M* | ND | NA | NA | NA |
| | **d** | | **Household heating and cooking - Biomass** | | | | | µg TEQ/t Ash |
| | | 1 | Contaminated biomass fired stoves<br>*LoC* | 1,500<br>*L* | ND | ND | NA | 1,000<br>*L* |
| | | 2 | Virgin biomass fired stoves (advanced technology)<br>*LoC* | 100<br>*M* | ND | ND | NA | 10<br>*M* |
| | | 3 | Straw fired stoves<br>*LoC* | 450<br>*L* | ND | ND | NA | 30<br>*L* |
| | | 4 | Charcoal fired stoves<br>*LoC* | 100<br>*L* | ND | ND | NA | 0.1<br>*L* |
| | | 5 | Open-fire (3-stone) stoves (virgin wood)<br>*LoC* | 20<br>*L* | ND | ND | NA | 0.1<br>*L* |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 6 | Simple stoves (virgin wood)<br>*LoC* | 100<br>*L* | ND | ND | NA | 0.1<br>*L* |
| | **e** | | **Domesting heating - Fossil fuels** | | | | | µg TEQ/t Ash |
| | | 1 | High chlorine coal/waste/biomass co-fired stoves<br>*LoC* | 1,700<br>*L* | ND | NA | NA | 5,000<br>*L* |
| | | 2 | Coal/waste/biomass co-fired stoves<br>*LoC* | 200<br>*L* | ND | NA | NA | NA |
| | | 3 | Coal fired stoves<br>*LoC* | 100<br>*M* | ND | NA | NA | 5<br>*M* |
| | | 4 | Peat fired stoves<br>*LoC* | 100<br>*M* | ND | NA | NA | NA |
| | | 4 | Oil fired stoves<br>*LoC* | 10<br>*M* | ND | NA | NA | NA |
| | | 5 | Natural gas fired stoves<br>*LoC* | 1.5<br>*M* | 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 |
| 4 | | | **Production of Mineral Products** | | | | | |
| | a | | **Cement kilns** | | | | | |
| | | 1 | Shaft kilns | 5 | ND | NA | ND | ND |
| | | | *LoC* | *H* | | | | |
| | | 2 | Old wet kilns, ESP temperature >300°C | 5 | ND | NA | ND | ND |
| | | | *LoC* | *H* | | | | |
| | | 3 | Rotary kilns, ESP/FF temperature 200 to 300°C | 0.6 | ND | NA | ND | ND |
| | | | *LoC* | *H* | | | | |
| | | 4 | Wet kilns, ESP/FF temperature <200°C and all types of dry kilns with preheater/precalciner, T<200°C | 0.05 | ND | NA | ND | ND |
| | | | *LoC* | *H* | | | | |
| | b | | **Lime** | | | | | |
| | | 1 | Cyclone/no dust control, contaminated or poor fuels | 10 | ND | NA | ND | ND |
| | | | *LoC* | *M* | | | | |
| | | 2 | Good dust abatement | 0.07 | ND | NA | ND | ND |
| | | | *LoC* | *H* | | | | |
| | c | | **Brick** | | | | | |
| | | 1 | No emission abatement in place and using contaminated fuels | 0.2 | NA | NA | 0.06 | 0.02 |
| | | | *LoC* | *H* | | | *H* | *H* |
| | | 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 | 0.02 | NA | NA | 0.006 | 0.002 |
| | | | *LoC* | *M* | | | *M* | *M* |
| | d | | **Glass** | | | | | |
| | | 1 | Cyclone/no dust control, contaminated or poor fuels | 0.2 | NA | NA | ND | ND |
| | | | *LoC* | *M* | | | | |
| | | 2 | Good dust abatement | 0.015 | NA | NA | ND | ND |
| | | | *LoC* | *M* | | | | |
| | e | | **Ceramics** | | | | | |
| | | 1 | Cyclone/no dust control, contaminated or poor fuels | 0.2 | NA | NA | ND | ND |
| | | | *LoC* | *M* | | | | |
| | | 2 | Good dust abatement | 0.02 | NA | NA | ND | ND |
| | | | *LoC* | *M* | | | | |
| | f | | **Asphalt mixing** | | | | | |
| | | 1 | Mixing plant with no gas cleaning | 0.07 | NA | NA | ND | ND |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | *LoC* | *M* | | | | |
| | | 2 | Mixing plant with fabric filter, wet scrubber | 0.007 | NA | NA | ND | 0.06 |
| | | | *LoC* | *M* | | | | *M* |
| | g | | **Oil shale processing** | | | | | |
| | | 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 |
| 5 | | | **Transport** | | | | | |
| | a | | **4-Stroke engines** | | | | | |
| | | 1 | Leaded fuel | 2.2 | NA | NA | NA | NA |
| | | | *LoC* | *H* | | | | |
| | | 2 | Unleaded gasoline without catalyst | 0.1 | NA | NA | NA | NA |
| | | | *LoC* | *M* | | | | |
| | | 3 | Unleaded gasoline with catalyst | 0.001 | NA | NA | NA | NA |
| | | | *LoC* | *M* | | | | |
| | | 4 | Ethanol with catalyst | 0.0007 | NA | NA | NA | NA |
| | | | *LoC* | *L* | | | | |
| | b | | **2-Stroke engines** | | | | | |
| | | 1 | Leaded fuel | 3.5 | NA | NA | NA | NA |
| | | | *LoC* | *L* | | | | |
| | | 2 | Unleaded fuel | 2.5 | NA | NA | NA | NA |
| | | | *LoC* | *L* | | | | |
| | c | | **Diesel engines** | | | | | |
| | | 1 | Regular Diesel | 0.1 | NA | NA | NA | ND |
| | | | *LoC* | *M* | | | | |
| | | 2 | Biodiesel | 0.07 | NA | NA | NA | ND |
| | | | *LoC* | *M* | | | | |
| | d | | **Heavy oil fired engines** | | | | | |
| | | 1 | All types | 2 | NA | NA | NA | ND |
| | | | *LoC* | *M* | | | | |

**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 |
| 6 | | | **Open Burning Processes** | | | | | |
| | a | | **Biomass burning** | | | | | |
| | | 1 | Agricultural residue burning in the field of cereal and other crops stubble, impacted, poor burning conditions | 30 | ND | 10 | NA | NA |
| | | | *LoC* | *M* | | *M* | | |
| | | 2 | Agricultural residue burning in the field of cereal and other crops stubble, not impacted | 0.5 | ND | 0.05 | NA | NA |
| | | | *LoC* | *M* | | *M* | | |
| | | 3 | Sugarcane burning | 4 | ND | 0.05 | NA | NA |
| | | | *LoC* | *H* | | *H* | | |
| | | 4 | Forest fires | 1 | ND | 0.15 | NA | NA |
| | | | *LoC* | *H* | | *H* | | |
| | | 5 | Grassland and savannah fires | 0.5 | ND | 0.15 | NA | NA |
| | | | *LoC* | *H* | | *H* | | |
| | b | | **Waste burning and accidental fires** | | | | | |
| | | 1 | Fires at waste dumps (compacted, wet, high organic carbon content) | 300 | ND | 10 | NA | NA |
| | | | *LoC* | *M* | | *M* | | |
| | | 2 | Accidental fires in houses, factories | 400 | ND | 400 | NA | NA |
| | | | *LoC* | *M* | | *M* | | |
| | | 3 | Open burning of domestic waste | 40 | ND | 1 | NA | NA |
| | | | *LoC* | *M* | | *M* | | |
| | | 4 | Accidental fires in vehicles (per vehicle) | 100 | ND | 18 | NA | NA |
| | | | *LoC* | *M* | | *M* | | |
| | | 5 | Open burning of wood (construction/demolition) | 60 | ND | 10 | NA | NA |
| | | | *LoC* | *M* | | *M* | | |

**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** | | | **Production and Use of Chemicals and Consumer Goods** | | | | | |
| | **a** | | **Pulp and paper mills *** | | | | | |
| | | | *Boilers (per ton ADt pulp)* | | | | | |
| | | 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* |
| | | | *Acqueous discharges and products* | | | | | |
| | | 1 | Kraft process, $Cl_2$, non-wood, PCP-contaminated fibers | | ND | | 30 | ND |
| | | | *LoC* | | | | *M* | |
| | | 2 | Kraft process, $Cl_2$ | | 4.5 | | 10 | 4.5 |
| | | | *LoC* | | *M* | | *M* | *M* |
| | | 3 | Mixed technology | | 1.0 | | 3 | 1.5 |
| | | | *LoC* | | *M* | | *M* | *M* |
| | | 4 | Sulfite process, $Cl_2$ | | ND | | 1 | ND |
| | | | *LoC* | | | | *M* | |
| | | 5 | Kraft process, $ClO_2$ | | 0.06 | | 0.5 | 0.2 |
| | | | *LoC* | | *M* | | *M* | *M* |
| | | 6 | Sulfite process, either $ClO_2$ 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** | | **Chlorinated Inorganic Chemicals** | | | | | |
| | | | *Elemental chlorine production (per ton ECU)* | | | | | |
| | | 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* |
| | c | | **Chlorinated Aliphatic Chemicals** | | | | | |
| | | | *ECD/VCM and EDC/VCM/PVC vent and liquid-vent combustors (per ton VCM)* | | | | | |
| | | | Low-End Technologies | 5 | | | | |
| | | | *LoC* | *L* | | | | |
| | | | Mid-Range Technologies | 0.5 | | | | |
| | | | *LoC* | *L* | | | | |
| | | | High-End Technologies | 0.05 | | | | |
| | | | *LoC* | *L* | | | | |
| | | | *ECD/VCM and EDC/VCM/PVC spent catalyst from facilties utilizing a fixed-bed oxychlorination catalyst (per ton EDC)* | | | | | |
| | | | Low-End Technologies | | | | | 8 |
| | | | *LoC* | | | | | *L* |
| | | | Mid-Range Technologies | | | | | 0.85 |
| | | | *LoC* | | | | | *L* |
| | | | High-End Technologies* | | | | | 0.02 |
| | | | *LoC* | | | | | *L* |
| | | | *ECD/VCM and EDC/VCM/PVC production processes (per ton EDC)* | | | | | |
| | | 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* |
| | | | *PVC only (per ton PVC product)* | | | | | |
| | | 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* |
| | d | | **Chlorinated Aromatic Chemicals (per ton product)** | | | | | |
| | | | *Chlorobenzenes* | | | | | |
| | | 1 | 1,4-Dichlorobenzene | ND | ND | NA | 39 | ND |
| | | | *LoC* | | | | *M* | |
| | | | *PCB* | | | | | |
| | | 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* | |
| | | | *PCP and PCP-Na* | | | | | |
| | | 1 | PCP | ND | ND | ND | 634,000 | ND |
| | | | *LoC* | | | | *M* | |
| | | 2 | PCP-Na | ND | ND | ND | 12,500 | ND |
| | | | *LoC* | | | | *M* | |
| | | | *2,4,5-T and 2,4,5-TCP* | | | | | |
| | | 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* | |
| | | | *Chloronitrofen (CNP)* | | | | | |
| | | 1 | Old technologies | ND | ND | ND | 9,200,000 | ND |
| | | | *LoC* | | | | *M* | |
| | | 2 | New technologies | ND | ND | ND | 4,500 | ND |
| | | | *LoC* | | | | *M* | |
| | | | *Pentachloronitrobenzene (PCNB)* | | | | | |
| | | 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* | |
| | | | *2,4-D and derivatives* | | | | | |
| | | 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* | |
| | | | *Chlorinated Paraffins* | | | | | |
| | | 1 | Low-End Technologies | ND | ND | ND | ND | ND |
| | | 2 | Mid-Range Technologies | ND | ND | ND | 500 | ND |
| | | | *LoC* | | | | *M* | |
| | | 3 | High-End Technologies | ND | ND | ND | 140 | ND |
| | | | *LoC* | | | | *M* | |
| | | | *P-chloranil* | | | | | |
| | | 1 | Direct chlorination of phenol | ND | ND | ND | 400,000 | ND |
| | | | *LoC* | | | | *M* | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 2 | Chlorination of hydroquinone with minimal purification<br>*LoC* | ND | ND | ND | 1,500,000<br>*M* | ND |
| | | 3 | Chlorination of hydroquinone with moderate purification<br>*LoC* | ND | ND | ND | 26,000<br>*M* | ND |
| | | 4 | Chlorination of hydroquinone with advanced purification<br>*LoC* | ND | ND | ND | 150<br>*M* | ND |
| | | | *Phthalocyanine dyes and pigments* | | | | | |
| | | 1 | Phthalocyanine copper<br>*LoC* | ND | ND | ND | 70<br>*M* | ND |
| | | 2 | Phthalocyanine green<br>*LoC* | ND | ND | ND | 1,400<br>*M* | ND |
| | | | *Dioxazine dyes and pigments* | | | | | |
| | | 1 | Blue 106<br>*LoC* | ND | ND | ND | 35,000<br>*M* | ND |
| | | 2 | Blue 108<br>*LoC* | ND | ND | ND | 100<br>*M* | ND |
| | | 3 | Violet 23<br>*LoC* | ND | ND | ND | 12,000<br>*M* | ND |
| | | | *Triclosan* | | | | | |
| | | 1 | Low-End Technologies<br>*LoC* | ND | ND | ND | 1,700<br>*M* | 82,000<br>*M* |
| | | 2 | Mid-Range Technologies<br>*LoC* | ND | ND | ND | 60<br>*M* | ND |
| | | 3 | High-End Technologies<br>*LoC* | ND | ND | ND | 3<br>*M* | ND |
| | e | | **Other Chlorinated and Non-Chlorinated Chemicals (per ton product)** | | | | | |
| | | | *$TiCl_4$ and $TiO_2$* | | | | | |
| | | 1 | Low-End Technologies<br>*LoC* | ND | 0.2<br>*M* | ND | 0<br>*M* | 42<br>*M* |
| | | 2 | Mid-Range Technologies<br>*LoC* | ND | 0.001<br>*M* | ND | 0<br>*M* | 8<br>*M* |
| | | | *Caprolactam* | | | | | |
| | | 1 | Caprolactam<br>*LoC* | 0.00035<br>*M* | 0.5 (pg TEQ/L)<br>*M* | ND | ND | ND |
| | f | | **Petroleum refining** | | | | | |
| | | 1 | Flares (per TJ fuel burned)<br>*LoC* | 0.25<br>*M* | NA | NA | NA | ND |
| | | | *Production processes (per ton oil)* | | | | | |
| | | 1 | Catalytic reforming unit<br>*LoC* | 0.02<br>*M* | NA | NA | NA | 14 (µg TEQ/t residue)<br>*M* |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 2 | Coking unit | 0.4 | NA | NA | NA | ND |
| | | | *LoC* | *M* | | | | |
| | | 3 | Refinery-wide wastewater treatment | ND | 5 (pg TEQ/L) | ND | ND | ND |
| | | | *LoC* | | *M* | | | |
| | **g** | | **Textile plants** | | | | | |
| | | 1 | Low-End Technologies | ND | ND | ND | 100 | ND |
| | | | *LoC* | | | | *L* | |
| | | 2 | Mid-Range, non-BAT Technologies | ND | ND | ND | 0.1 | ND |
| | | | *LoC* | | | | *L* | |
| | | 3 | High-End, BAT Technologies | NA | NA | NA | NA | NA |
| | **h** | | **Leather plants** | | | | | |
| | | 1 | Low-End Technologies | NA | ND | ND | 1,000 | ND |
| | | | *LoC* | | | | *L* | |
| | | 2 | Mid-Range Technologies | NA | ND | ND | 10 | ND |
| | | | *LoC* | | | | *L* | |

* 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 |
| 8 | | | **Miscellaneous** | | | | | |
| | **a** | | **Drying of biomass** | | | | | |
| | | 1 | Highly contaminated fuel (PCP treated) | 10 | NA | ND | 0.5 | 2,000 |
| | | | *LoC* | *L* | | | *L* | *L* |
| | | 2 | Moderately contaminated fuel | 0.1 | NA | ND | 0.1 | 20 |
| | | | *LoC* | *L* | | | *L* | *L* |
| | | 3 | Clean fuel | 0.01 | NA | ND | 0.1 | 5 |
| | | | *LoC* | *L* | | | *L* | *L* |
| | **b** | | **Crematoria** | | | | | |
| | | 1 | No control (per cremation) | 90 | NA | NA | NA | ND |
| | | | *LoC* | *H* | | | | |
| | | 2 | Medium control or open air cremations (per cremation) | 10 | NA | NA | NA | 2.5 |
| | | | *LoC* | *M* | | | | *M* |
| | | 3 | Optimal control (per cremation) | 0.4 | NA | NA | NA | 2.5 |
| | | | *LoC* | *L* | | | | *L* |
| | **c** | | **Smoke houses** | | | | | |
| | | 1 | Contaminated fuels | 50 | NA | ND | ND | 2,000 |
| | | | *LoC* | *L* | | | | *L* |
| | | 2 | Clean fuels, no afterburner | 6 | NA | ND | ND | 20 |
| | | | *LoC* | *L* | | | | *L* |
| | | 3 | Clean fuels, afterburner | 0.6 | NA | ND | ND | 20 |
| | | | *LoC* | *L* | | | | *L* |
| | **d** | | **Dry cleaning** | | | | | |
| | | 1 | Heavy textiles, PCP-treated, etc. | NA | NA | NA | NA | 3,000 |
| | | | *LoC* | | | | | *L* |
| | | 2 | Normal textiles | NA | NA | NA | NA | 50 |
| | | | *LoC* | | | | | *L* |
| | **e** | | **Tobacco smoking** | | | | | |
| | | 1 | Cigar (per million cigars) | 0.3 | NA | NA | NA | 0.3 |
| | | | *LoC* | *L* | | | | *L* |
| | | 2 | Cigarette (per million cigarettes) | 0.1 | NA | NA | NA | 0.1 |
| | | | *LoC* | *L* | | | | *L* |

**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 |
| 9 | | | **Disposal and Landfill** | | | | | |
| | **a** | | **Landfills, Waste Dumps and Landfill Mining** | | | | | |
| | | 1 | Hazardous wastes | NA | 5 | NA | NA | NA |
| | | | *LoC* | | *L* | | | |
| | | 2 | Mixed wastes | NA | 0.5 | NA | NA | 50 |
| | | | *LoC* | | *L* | | | *L* |
| | | 3 | Domestic wastes | NA | 0.05 | NA | NA | 5 |
| | | | *LoC* | | *L* | | | *L* |
| | **b** | | **Sewage and sewage treatment (per ton d.m.*)**<br>*** for water releases, units are in pg TEQ/L** | | | | | |
| | | 1 | Mixed domestic and specific industrial inputs | | | | | |
| | | | No sludge removal | NA | 10 | NA | NA | NA |
| | | | With sludge removal | NA | 1 | NA | NA | 200 |
| | | | *LoC* | | *H* | | | *H* |
| | | 2 | Urban and industrial inputs | | | | | |
| | | | No sludge removal | NA | 1 | NA | NA | NA |
| | | | With sludge removal | NA | 0.2 | NA | NA | 20 |
| | | | *LoC* | | *H* | | | *H* |
| | | 3 | Domestic inputs | | | | | |
| | | | No sludge removal | NA | 0.04 | NA | NA | NA |
| | | | With sludge removal | NA | 0.04 | NA | NA | 4 |
| | | | *LoC* | | *H* | | | *H* |
| | **c** | | **Open water dumping (per m$^3$)** | | | | | |
| | | 1 | Mixed domestic and industrial wastewater | NA | 0.005 | NA | NA | NA |
| | | | *LoC* | | *L* | | | |
| | | 2 | Urban and peri-urban wastewater | NA | 0.0002 | NA | NA | NA |
| | | | *LoC* | | *L* | | | |
| | | 3 | Remote environments | NA | 0.0001 | NA | NA | NA |
| | | | *LoC* | | *L* | | | |
| | **d** | | **Composting (per ton d.m.)** | | | | | |
| | | 1 | Organic wastes separated from mixed wastes | NA | NA | NA | 50 | NA |
| | | | *LoC* | | | | *H* | |
| | | 2 | Clean compost | NA | NA | NA | 5 | NA |
| | | | *LoC* | | | | *H* | |
| | **e** | | **Waste oil disposal** | | | | | |
| | | 1 | 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) |
|---|---|---|---|---|
| **10** | | | **Contaminated Sites and Hotspots** | |
| | **a** | | **Production sites of chlorine** | |
| | | 1 | Chlor-alkali production | |
| | | 2 | Leblanc process and associated chlorine/bleach production | |
| | **b** | | **Production sites of chlorinated organics** | |
| | | 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 | |
| | **c** | | **Application sites of PCDD/PCDF containing pesticides and chemicals** | |
| | **d** | | **Timber manufacture and treatment stes** | |
| | **e** | | **Textile and leather factories** | |
| | **f** | | **Use of PCB** | |
| | **g** | | **Use of chlorine for production of metals and inorganic chemicals** | |
| | **h** | | **Waste incinerators** | |
| | **i** | | **Metal industries** | |
| | **j** | | **Fire accidents** | |
| | **k** | | **Dredging of sediments and contaminated flood plains** | |
| | **l** | | **Dumps of wastes/residues from groups 1-9** | |
| | **m** | | **Kaolin or ball clay sites** | |

# 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 | | | | | |
| **TOTAL** | 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** |
|---|---|---|---|
| **1. Waste incineration** | | | |
| 1a. Municipal solid waste incineration | Part II (a) | 090201 | 6C |
| 1b. Hazardous waste incineration | Part II (a)<br>Part II (b) | 090202,<br>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,<br>090202 | 6C |
| 1g. Destruction of animal carcasses | Part III (i) | 090902 | 6C |
| **2.Ferrous and non-ferrous metal production** | | | |
| 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,<br>040205,<br>040206,<br>040207 | 1A2a<br>2C1 |
| Foundries | Part III (b) | 030303 | 1A2a |
| 2d. Copper production | Part II (d) (i) | 030306,<br>030309 | 1A2b, 2C5a |
| 2e. Aluminum production | Part II (d)(iii) | 030310<br>030322,<br>040301 | 1A2b<br>2C3 |
| 2f. Lead production | Part III (b) | 030304,<br>030307 | 1A2b, 2C5b |
| 2g. Zinc production | Part II (d)(iv) | 030305,<br>030308,<br>040309 | 1A2b, 2C5d |
| 2h. Brass and bronze production | Part III (b) | 030326,<br>040309 | 1A2b |
| 2i. Magnesium production | Part III (b) | 030323 | 1A2b |
| 2j. Other non-ferrous metal production | Part III (b) | 030326,<br>040309 | 1A2b, 2C5e |
| 2k. Shredders | Part III (k) | | |
| 2l. Thermal wire reclamation | Part III (l) | 030307,<br>030309 | 1A2b |
| **UNEP Dioxin/Furan Toolkit** | **Stockholm Convention Annex C** | **SNAP 97** | **NFR** |
| **3. Power generation and heating/cooking** | | | |

| | | | |
|---|---|---|---|
| 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 |
| **4. Production of mineral products** | | | |
| 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 |
| **5. Transport** | | | |
| 5a. 4 –Stroke engines | Part III (h) | 0701, 0702, 0703,0704,0705 | 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 |
| **UNEP Dioxin/Furan Toolkit** | **Stockholm Convention Annex C** | **SNAP 97** | **NFR** |
| **6. Open burning** | | | |

| | | | |
|---|---|---|---|
| 6a. Biomass burning:<br>Forest fires<br>Savanah burning<br>Agriculture residue burning | Part III (a) | 110301,<br>110302<br>100301-05 | 11B<br>4E<br>4F |
| 6b. Waste burning, accidental fire | Part III (a) | 0907 | 6D |
| **7. Production and use of chemicals and consumer goods** | | | |
| 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 |
| **8. Miscellaneous** | | | |
| 8a. Drying of biomass | | | |
| 8b. Crematoria | Part III (g) | 090901 | 6C |
| 8c. Smoke houses | | | |
| 8d. Dry cleaning | Part III (f) | 060202 | 3B2 |
| 8e. Tobaco smoking | | | |
| **9. Disposal** | | | |
| 9a. Landfills and waste dumps | | 090401,<br>090402 | 6A |
| 9b. Seawage and seawage treatment | | 091001,<br>091002 | 6B |
| 9c. Open water dumping | | 091001 | 6B |
| 9d. Composting | | 091005 | 6D |
| 9e. Waste oil treatment | Part III (m) | 091008 | 6D |
| **UNEP Dioxin/Furan Toolkit** | **SC Article 6** | **SNAP 97** | **NFR** |
| **10. Identification of potential hotspots** | | | |
| 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,<br>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).<br>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 Farenheit). 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 intable III.7.1; most countries have used the emission factors from the 2$^{nd}$ 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 |
| **45%** | **2%** | **11%** | **8%** | **34%** |
| **Grand total (ca.)** | | **58,500** | | |

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 (µg 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.

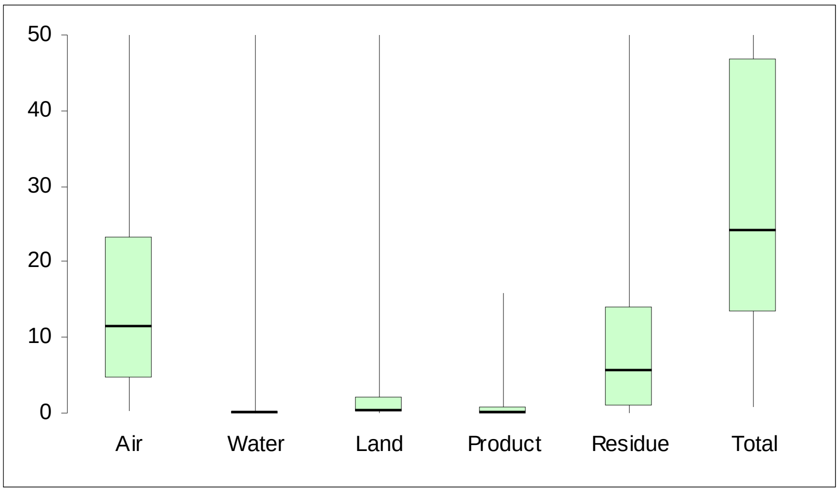

**Figure III.7.1 Graphical sketch for PCDD/PCDF releases per and per year (μg TEQ per person per year)**

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%

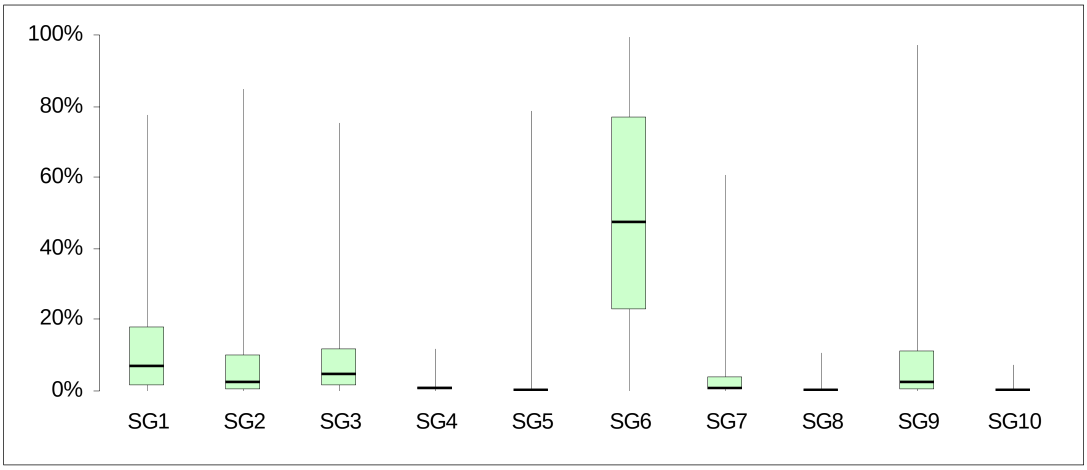

**Figure III.7.2 Statistical evaluation of importance of source groups (n=67)**

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.

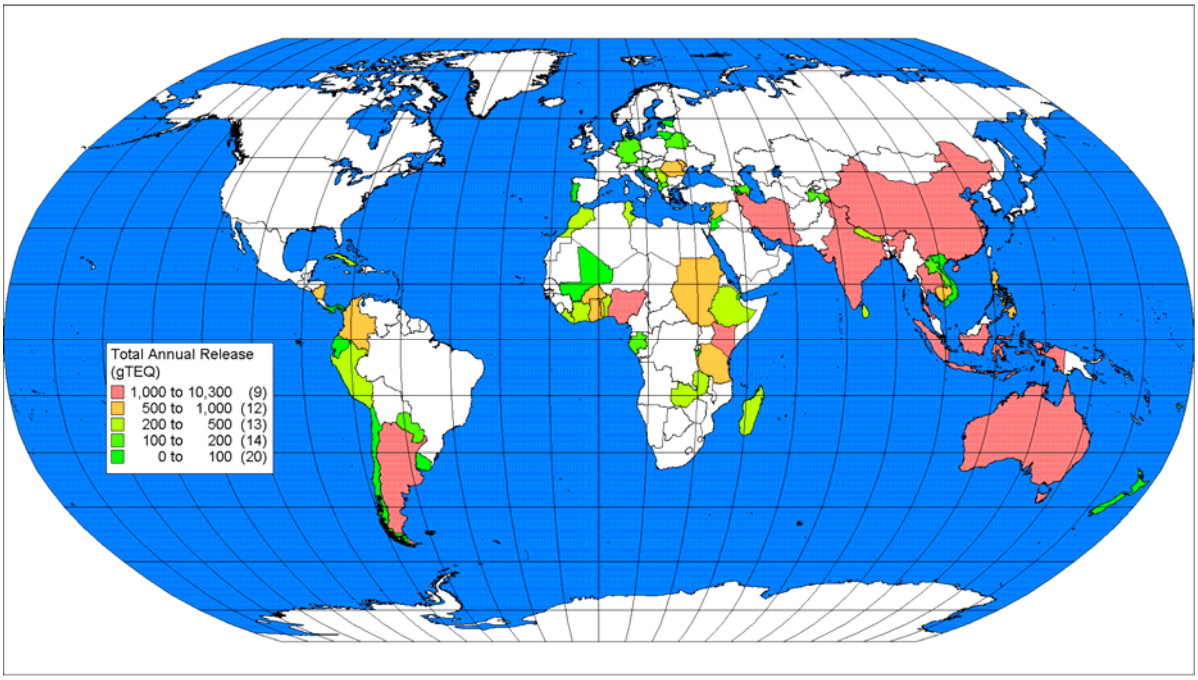

**Figure III.7.3 Total annual release per country (g TEQ/a)**

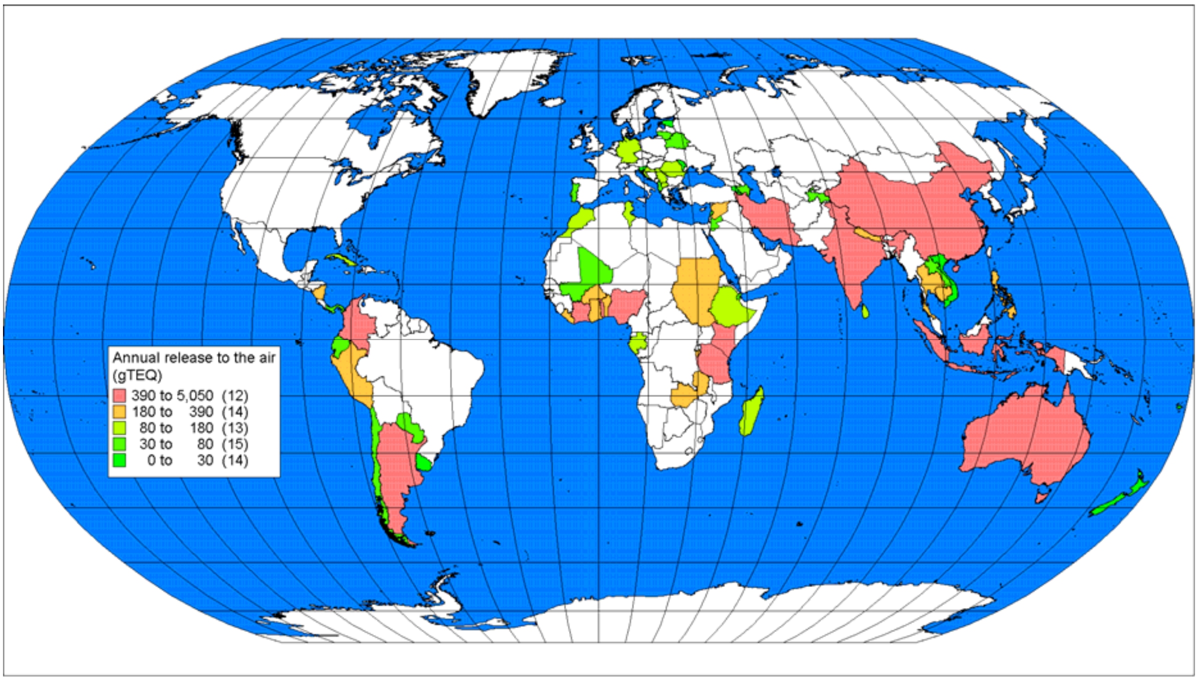

**Figure III.7.4 Total annual release to air per country (g TEQ/a)**

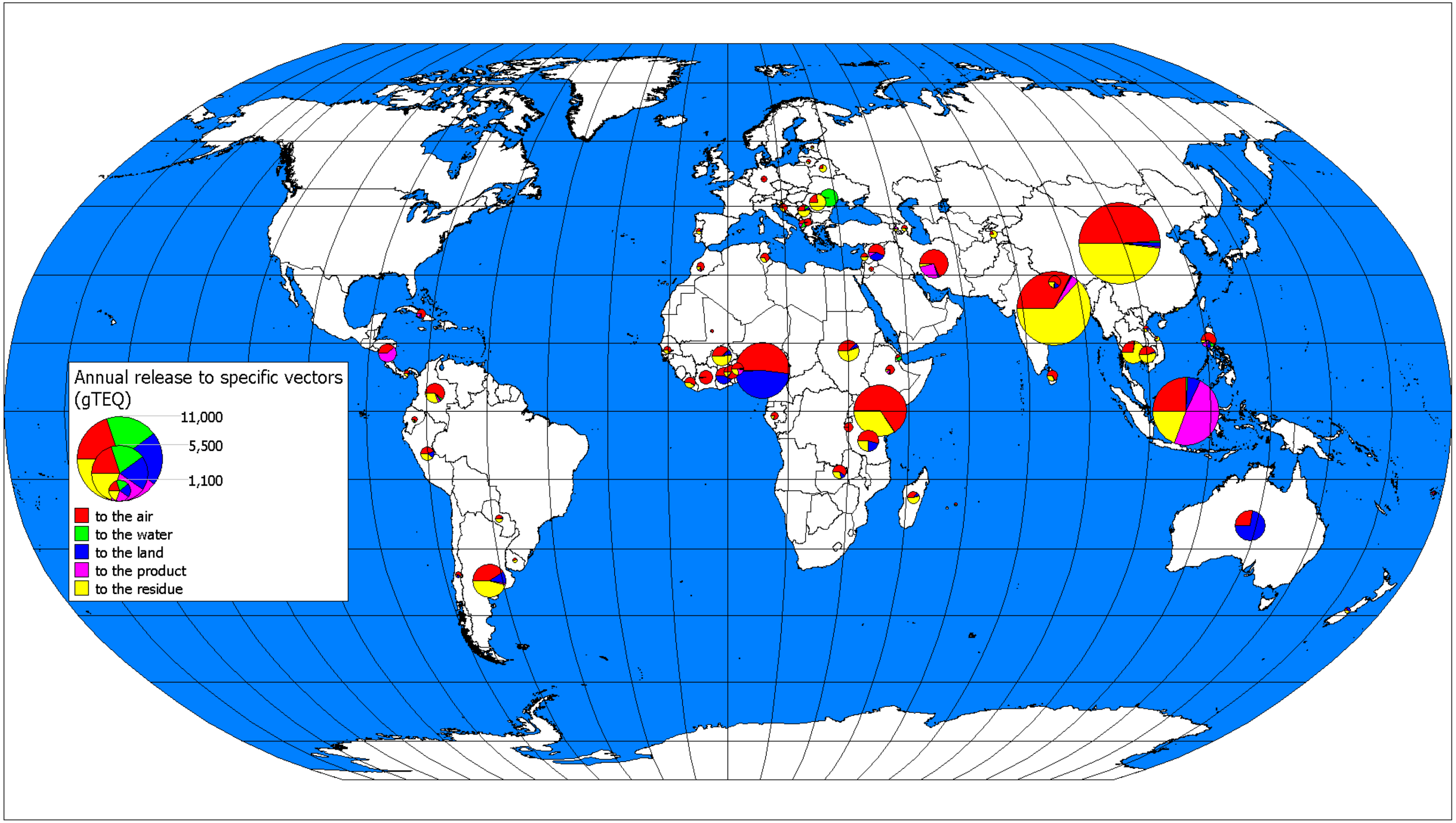

**Figure III.7.5 Total annual release per country and vector (g TEQ/a)**

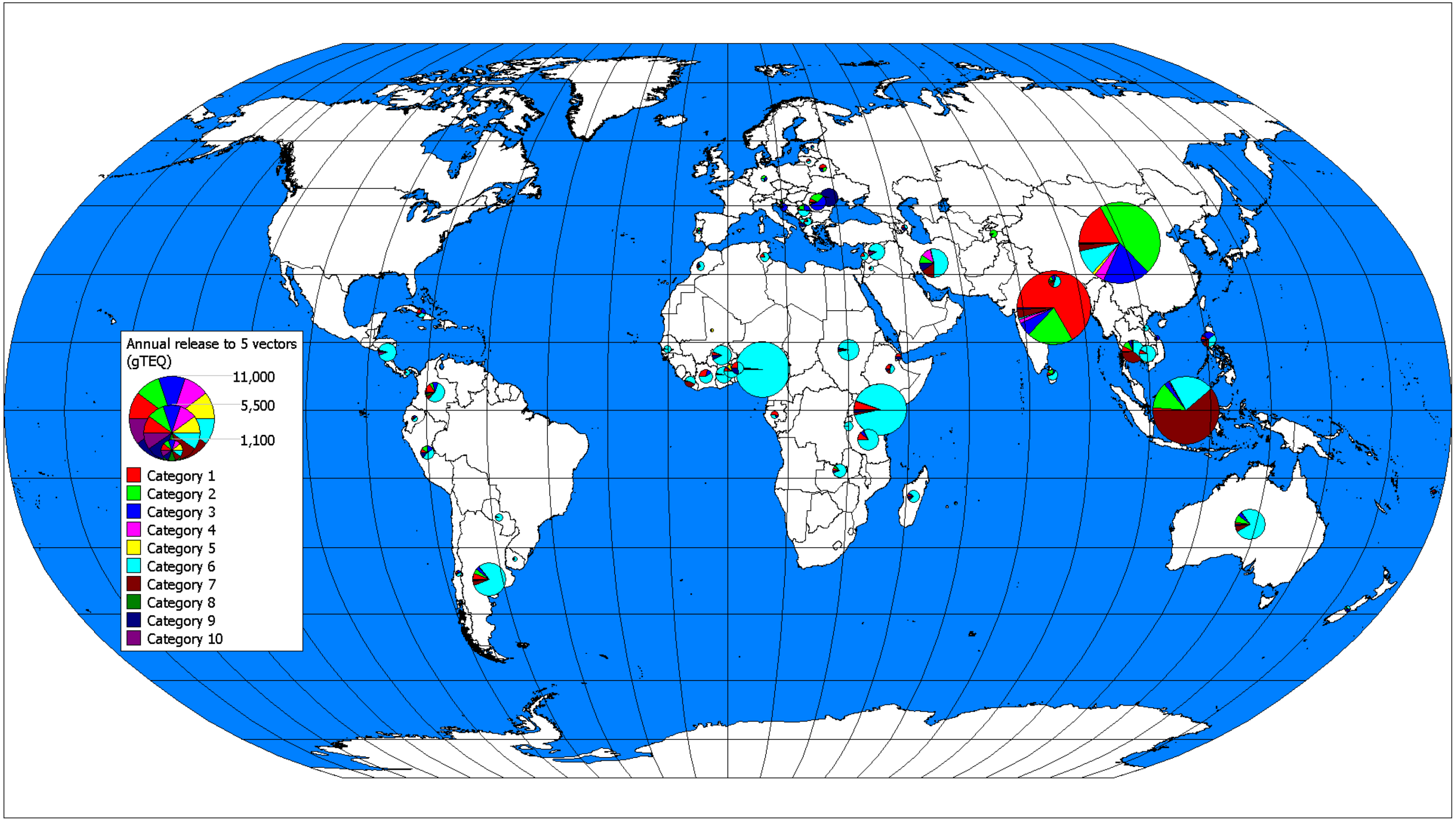

**Figure III.7.6 Total annual release per country and source group (g TEQ/a)**

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.

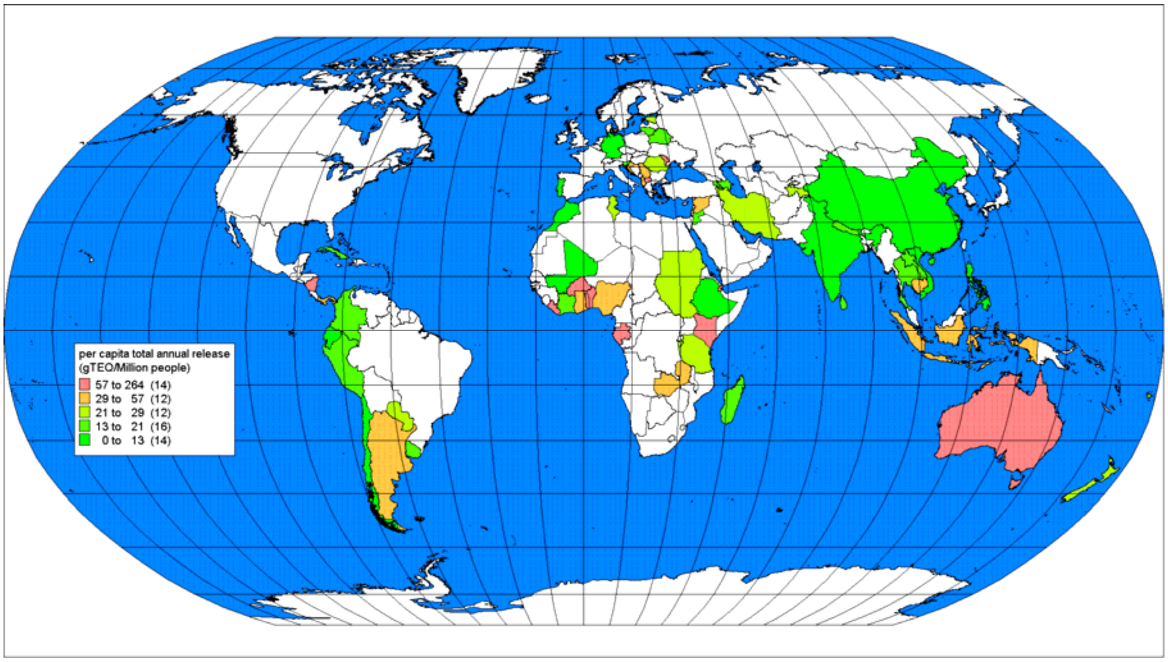

**Figure III.7.7 Per capita total annual release (μg TEQ/a)**

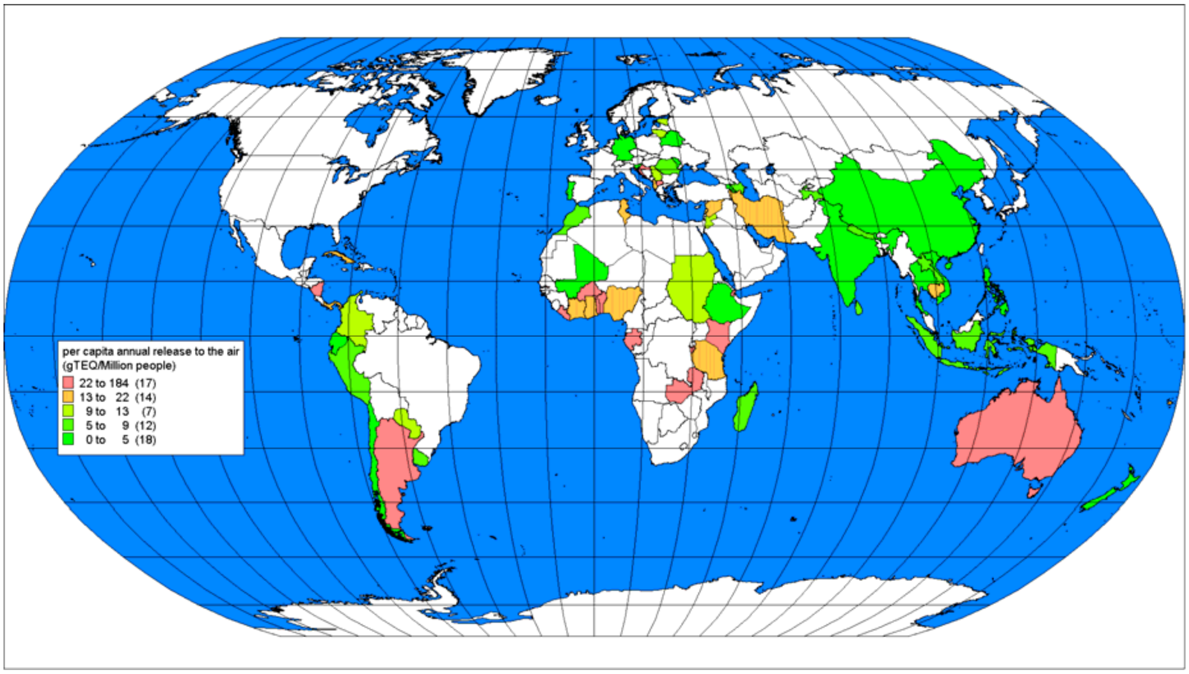

**Figure III.7.8 Per capita annual release to air (μg TEQ/a)**

Finally, the releases per unit area (km$^2$) is shown in Figure III.7.9 and based on *per capita* gross domestic product in Figure III.7.10.

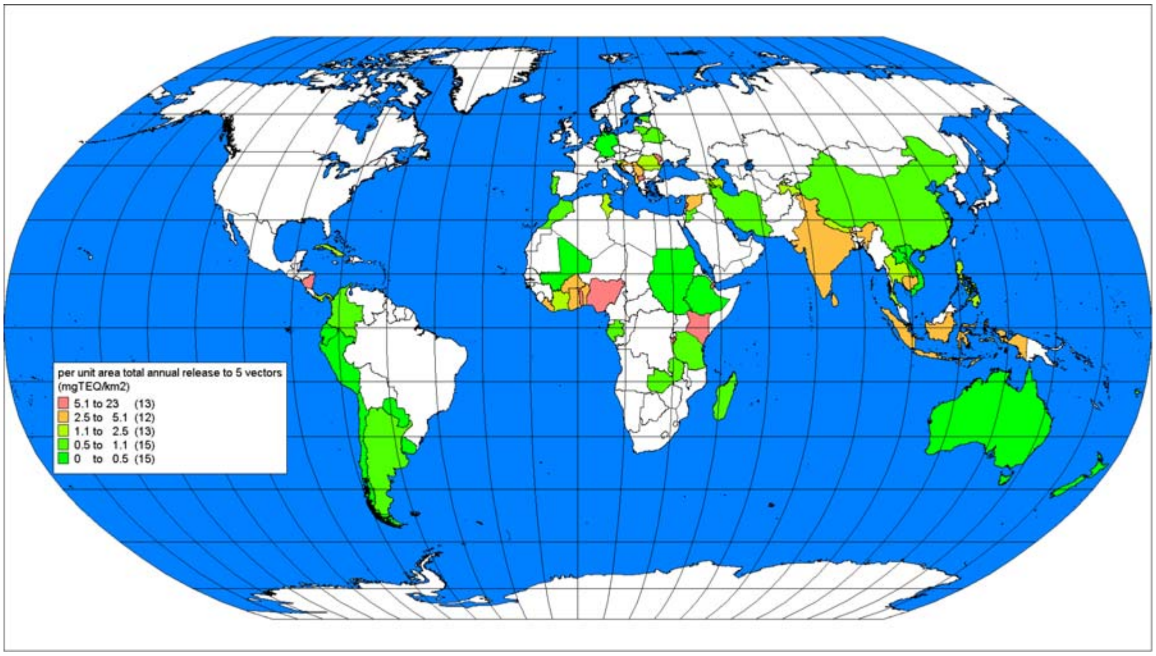

**Figure III.7.9 Total annual release per square kilometer (μg TEQ/km$^2$)**

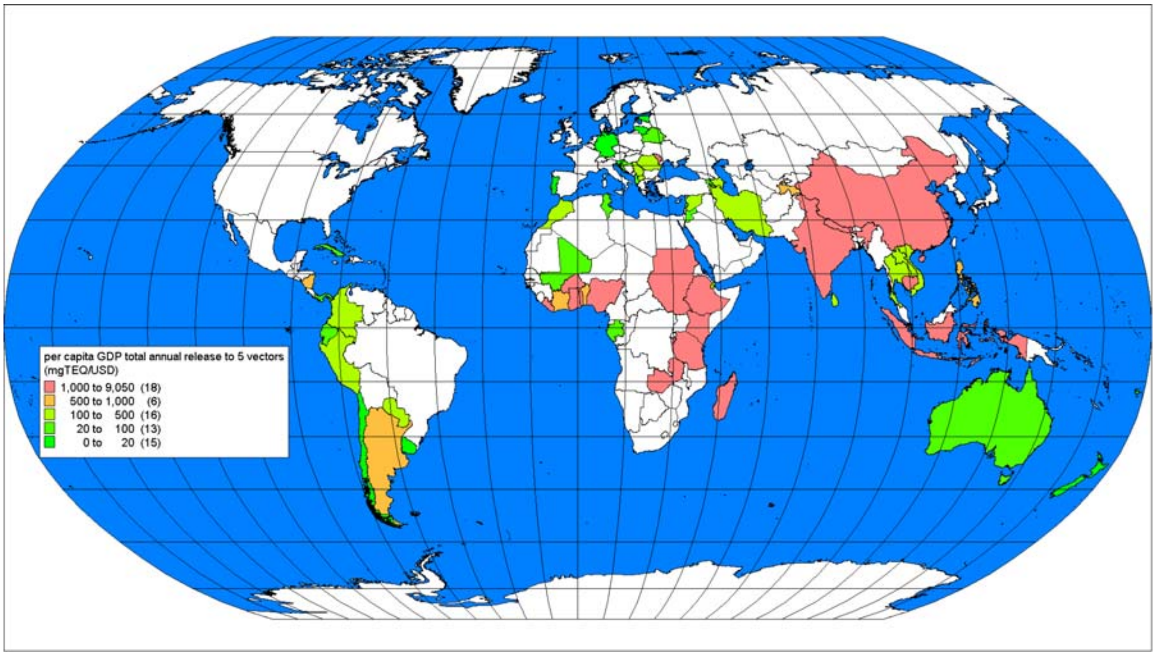

**Figure III.7.10 Total annual releases according to per capita GDP (mg TEQ/USD person)**

# 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** |
|---|---|
| **High** | Peer review<br>Low data range<br>Broad geographical coverage<br>Assumptions and/or expert judgment are not required<br>High stability of the process |
| **Medium** | Any combination of high and low criteria |
| **Low** | No peer review<br>Wide data range<br>Limited geographical coverage<br>Extrapolation is needed *e.g*. EF derived from similar class<br>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 $Nm^3$/t MSW and a concentration of 350 ng TEQ/$Nm^3$ (at 11% $O_2$). 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 $Nm^3$/t MSW, due to better combustion controls and lower excess air and the PCDD/PCDF concentration is reduced to 50 ng TEQ/$Nm^3$ (at 11% $O_2$). 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/$Nm^3$ (at 11% $O_2$). Also, the specific flue gas volume is reduced to 6,000 $Nm^3$/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 $Nm^3$/t MSW and a concentration of less than 0.1 ng TEQ/$Nm^3$ (at 11% $O_2$) will be the norm (LUA 1997, IFEU 1998).

In a study of a Thai municipal solid waste incinerator, the flue gas concentrations at 11% $O_2$ ranged from 0.65 to 3.10 ng I- TEQ/$Nm^3$ with an average of 1.71 ng TEQ/$Nm^3$ (at 11% $O_2$). The concentrations of total PCDD/PCDF ($Cl_4$-$Cl_8$) were between 41.3 and 239 with a mean of 122 ng/$Nm^3$ (at 11% $O_2$) (UNEP 2001, Fiedler *et al*. 2002). The measured average concentration of 122 ng PCDD/PCDF/$m^3$ is above the Thai standard for municipal waste incinerators of 30 ng/$m^3$; the mean of 1.7 ng TEQ/$Nm^3$ is also above the European standard of 0.1 ng TEQ/$m^3$. 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/Nm³ (at 11% $O_2$), 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 Nm³/t of hazardous waste and a concentration of about 2,000 ng TEQ/Nm³.

Class 2 assumes a reduction in the specific flue gas volume flow rate to 15,000 Nm³/t of hazardous waste due to better combustion controls and lower excess air. The PCDD/PCDF concentration drops to 20 ng TEQ/Nm³ (at 11% $O_2$) 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/Nm³ (at 11% $O_2$). Also, the specific flue gas volume flow rate is reduced to 10,000 Nm³/t HW.

Class 4 represents the current state-of-the-art in HW incineration and APC technology. Thus, only 7,500 Nm³/t HW and a concentration of significantly less than 0.1 ng TEQ/Nm³ (at 11% $O_2$) 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, how-ever, 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/Nm³ (at 11% $O_2$) 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 Nm³/t medical wastes burned and a concentration of about 2,000 ng TEQ/Nm³ (at 11% $O_2$).

Class 2 assumes a reduction in the specific flue gas volume flow rate to 15,000 Nm³/t medical wastes due to better combustion controls and lower excess air. The PCDD/PCDF concentration drops to 200 ng TEQ/Nm³ (at 11% $O_2$) in this case.

Class 3 is based on European data where a concentration of 35 ng TEQ/Nm³ (at 11% $O_2$) with 15,000 Nm³/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 $Nm^3$/t of medical waste was generated and a concentration of less than 0.1 ng TEQ/$Nm^3$ (at 11% $O_2$) 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% $O_2$ – were between 21.8 and 43 ng TEQ/$Nm^3$ for line A and between 10.7 and 45.0 ng TEQ/$Nm^3$ for line B; the averages were 33.8 and 28.6 ng TEQ/$Nm^3$, 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/Nm³ (at 11% $O_2$) 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 Nm³/t light-shredder waste and a concentration of less than 0.1 ng TEQ/Nm³ (at 11% $O_2$) 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$^3$ (11% $O_2$) (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/Nm³ (at 11% $O_2$) and a specific flue gas volume flow rate of about 12,500 Nm³/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/Nm³ (at 11% $O_2$) (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 (µg 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 (µg/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 $Nm^3$ per ton of sinter and a concentration of 10 ng TEQ/$Nm^3$ (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/$m^3$ (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 $Nm^3$/t and a concentration of 0.2 ng TEQ/$Nm^3$ (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/$Nm^3$ (Kim *et al*. 2005), which corresponds to an emission factor of 0.9 µg TEQ/t (assuming a gas flow of 2,000 $Nm^3$/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/$Nm^3$ (Guerriero *et al*. 2006), which, assuming a gas flow of 2,000 $Nm^3$/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/$Nm^3$ (Kim *et al*. 2005). Assuming a gas flow of 2000 $Nm^3$/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 (µg 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 (µg/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 µg 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 µg 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** |
| **Iron and Steel Making** | | | | | | |
| 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,<br>b. BOF furnaces | **0.001** | | | | |
| 4 | Blast furnaces with APCS | **0.001** | | | | |
| **Iron foundries** | | | | | | |
| 1 | Cold air cupola [or hot air cupola] or rotary drum with no gas cleaning | | | | | |
| 2 | Rotary Drum - fabric filter | **0.5** | | | | |
| 3 | Cold air cupola – fabric filter [or wet scrubber] | **0.5** | | | | **0.1** |
| 4 | Hot air cupola, or induction furnace – fabric filter | **0.02** | | | | **0.01** |

**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** |
| **Iron and Steel Making** | | | | | | |
| 1 | Dirty scrap (cutting oils, general contamination), scrap preheating, limited controls | **2500** | | | | |
| 2 | Clean scrap/virgin iron or dirty scrap, afterburner and fabric filter | **2500** | | | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| 3 | a. Clean scrap/virgin iron or dirty scrap, EAF equipped with APCS designed for low PCDD/PCDF emission,<br>b. BOF furnaces | **2 BOF**<br>**2500 EAF** | | | | |
| 4 | Blast furnaces with APCS | **1** | | | | |

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$^3$ 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$^3$/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$^3$ 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$^3$ (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 theses 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$^3$ were measured in the flue gases from four installations (LUA 1997); the median was 0.016 ng I-TEQ/Nm$^3$. The Danish inventory utilized the German data and a stack volume of 33,000 Nm$^3$ 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$^3$ - 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) | | | | |
|---|---|---|---|---|---|---|
| | **Classification** | **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/Nm³ (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/Nm³ with a geometric mean of 0.11 ng

TEQ/Nm³ (German data, LUA 1997). The compilation for European plants by the IPPC Bureau reported emissions of <0.1 ng I-TEQ/Nm³ (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/Nm³ 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/Nm³ 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/Nm³ and 0.3 ng I-TEQ/Nm³ whereas the higher concentrations were obtained when PVC was present in the recycled materials. Purified gases after the $H_2SO_4$ plant were either non-quantifiable or 0.001 ng I-TEQ/Nm³. The EU Dioxin Inventory report of 1997 (LUA 1997) reports concentrations of 0.005-0.015 ng I-TEQ/m³ in the waste gases from the roasting furnace for ore desulphurization. The volume of the waste gas was 5,000 Nm³ per ton of copper produced. In addition, from a Swedish primary smelter that recycles considerable amounts of secondary materials, which produced 2,000 Nm³/t of waste gases, a concentration of 11 ng I-TEQ/m³ 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$^3$ 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$^3$. Assuming a gas flow of 10,000 Nm$^3$/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$^3$, 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$^3$ 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$^3$/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 ($H_2SO_4$ 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$^3$ 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$^3$. 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$^3$ (Kim *et al*. 2005, François *et al*. 2005). Assuming a gas flow of

10,000 $Nm^3$/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/$Nm^3$. 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 (µg 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 (µg/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$^3$ 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$^3$ 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 (µg TEQ/t lead) | | | | |
|---|---|---|---|---|---|---|
| | **Classification** | **Air** | **Water** | **Land** | **Product** | **Residue** |
| 1 | Lead production from scrap containing PVC | **2** | | | | |
| 2 | Lead production from PVC/Cl2 free scrap, some APCS | **0.2** | | | | **0.1** |
| 3 | Lead production from PVC/Cl2 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 (µg/t lead) | | | | |
|---|---|---|---|---|---|---|
| | **Classification** | **Air** | **Water** | **Land** | **Product** | **Residue** |
| 1 | Lead production from scrap containing PVC | **1,000** | | | | |
| 2 | Lead production from PVC/Cl2 free scrap, some APCS | **1,000** | | | | |
| 3 | Lead production from PVC/Cl2 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 µg TEQ/t lead, reverberatory/co-located furnace = 0.05-0.41 µg TEQ/t lead, and rotary furnace = 0.24-0.66 µg 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 ng TEQ/m³ for blast furnaces before and after the scrubber, respectively; 0.41 and 0.05 ng TEQ/m³ for reverberatories/collocated furnaces before and after the scrubbers, respectively; and 0.24 and 0.66 ng TEQ/m³ for rotary kilns before and after the scrubbers, respectively.

European measurements gave 5 µg 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 ng TEQ/m³ were measured). German measurements were 0.14-0.27 ng TEQ/Nm³ at rotary kilns; 0.59 ng TEQ/Nm³ at a shaft furnace, 0.09-0.18 ng TEQ/Nm³ at short rotary kilns and 0.14-0.27 ng TEQ/Nm³ at rotary kilns. A recycling lead smelter for used car batteries had emissions between 0.2 and 0.3 ng TEQ/Nm³. 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 µg 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 ng I-TEQ/m³ with a mean of 0.027 ng I-TEQ/m³ for the line with the combined flue gas streams and from 0.06 to 0.11 ng I-TEQ/m³ with a mean of 0.089 ng I-TEQ/m³ for line, which only operated the rotary kiln at the operational $O_2$ content of about 19%. The latter concentration corresponds to an emission factor of 10 µg TEQ/t of lead and therefore very well fits into class 2 (EF = 8 µg TEQ/t of lead). Concentrations measured in China (Ba *et al*. 2009) led to an emission factor estimate of 0.64 µg TEQ/t. The one calculated from measurements carried out in South Korea reaches 3.14 µg TEQ/t (Yu *et al*. 2006). The CORINAIR database provides a higher emission factor of 20 µg 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 µg TEQ/t (Iwata *et al*. 2008).

An emission factor of 8 µg 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 µg 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 µg TEQ/t for high technology furnaces and sophisticated flue gas cleaning equipment including scrubbers (concentrations well below 0.1 ng TEQ/m³).

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 | **100** | | | | |
| 2 | Hot briquetting/rotary furnaces, basic dust control; *e.g.*, fabric filters/ESP | **2** | | | | **3** |
| 3 | Comprehensive pollution controls, *e.g.*, fabric filters with active carbon/DeDiox technology | **0.1** | | | | |
| 4 | Zinc melting and primary zinc production | **0.001** | | | | |

**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 | **50,000** | | | | |
| 2 | Hot briquetting/rotary furnaces, basic dust control; *e.g.*, fabric filters/ESP | **50,000** | | | | |
| 3 | Comprehensive pollution controls, *e.g.*, fabric filters with active carbon/DeDiox technology | **50,000** | | | | |
| 4 | Zinc melting and primary zinc production | **1,000** | | | | |

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 µg TEQ/t zinc with emissions between 89 and 953 ng TEQ/m³, mean = 521 ng TEQ/m³), a rotating cylinder furnace (62.3 µg TEQ/t with emissions between 10 and 335 ng TEQ/m³; mean = 175 ng TEQ/m³) and for zinc melting (typically under 0.1 ng TEQ/m³ (LUA 1997).

Although this data set is very limited initial estimations of releases may be obtained by applying the emission factor of 100 µg 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 µg 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 µg 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 µg 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 µg TEQ/t). It also measured an emission factor of 5 µg 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 µg 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 µg 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 µg/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 µg/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 (µg/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, *e.g*. 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$^3$ with an average of 0.15 ng I-TEQ/Nm$^3$ at the actual operating $O_2$ concentration of 19%. This concentration corresponds to an emission factor of 11 µg I-TEQ/t of brass (11 µg WHO-TEQ/t). Hence, an emission factor of 10 µg 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 µg 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$^3$, corresponding to an emission factor range of 0.03 to 0.14 µg TEQ/t (Merz 2004).

As far as HCB is concerned, the Japanese study provides an emission factor value of 9,400 µg/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 Cl2 – no treatment on effluent, limited gas treatment | | | | | |
| 2 | Production using MgO/C thermal treatment in Cl2 – 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 Cl2 – no treatment on effluent, limited gas treatment | | | | | |
| 2 | Production using MgO/C thermal treatment in Cl2 – 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$^3$ 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$^3$ 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$^3$ 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 $Cl_2$.

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 NiCl2 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/m³ (class 2) to tens of ng/m³ (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 (µg 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 µg TEQ/t (concentration of 0.04-0.4 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 ng TEQ/Nm$^3$ and 0.023 ng TEQ/Nm$^3$ (10 samples) were measured respectively. Assuming a production of 80 t/h and a gas flow of 65,000 Nm$^3$/h, such concentrations would correspond to emission factors ranging from 0.019 to 0.30 µg 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 ng TEQ/Nm$^3$ which would correspond to a mean emission factor of 0.32 µg TEQ/t. The Swedish one (10 samples) show concentrations ranging from 0.29 to 0.94 ng TEQ/Nm$^3$, corresponding to a mean emission factor of 0.45 µg TEQ/t of recovered steel. Therefore, a PCB emission factor of 0.4 µg 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 2l Thermal Wire Reclamation and E-waste Recycling

## Overview of recent revisions

Category 2l 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 2l Thermal Wire Reclamation and E-waste Recycling**

| 2l Thermal Wire Reclamation and E-waste Recycling | | Emission Factors (µg TEQ/t material) | | | | |
|---|---|---|---|---|---|---|
| | **Classification** | **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/m³ (Dutch data) and emission factors up to 500 µg TEQ/t were used in the Dutch and Austrian inventories (LUA 2000); lowest were 3.3 µg TEQ/t. The Swiss inventory applied an emission factor of 2,340 µg 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 µg 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 µg TEQ/t and 100 µg 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 µg 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 µg 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<br>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**

| **Energy** | | **Corresponds to:** | |
|---|---|---|---|
| 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 $10^{-6}$ | Terajoule (TJ) |
| Gigawatt hour (GWh) | 1 | 3.6 | Terajoule (TJ) |
| Terajoule (TJ) | 1 | 2,777,777,778 | Kilowatt hour (kWh) |
| **Power** | | | |
| 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**

| **WEC* Standard Energy Units** | equals | |
|---|---|---|
| 1 tonne of oil equivalent (toe) ** | 42 000 | MJ (net calorific value) |
| 1 tonne of coal equivalent (tce) | 29300 | MJ (net calorific value) |
| **Representative Average Conversion Factors** | | |
| 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 |
| **Electricity** | | |
| 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 ($m^3$). 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 $m^3$ 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 $m^3$ of natural gas into tons; a conversion factor of 0.0000008 must be used to convert liters of natural gas into tons;
- 1 $m^3$ 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 $m^3$ 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 ($O_2$ ref = 6%) | SFV = 350 $Nm^3/GJ$ |
| Fuel oil ($O_2$ ref = 3%) | SFV = 280 $Nm^3/GJ$ |
| Natural gas ($O_2$ ref = 3%) | SFV = 270 $Nm^3/GJ$ |

(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 $O_2$ ref = 5% | SFV = 315 $Nm^3/GJ$ |
| Stationary gas turbines burning domestic oil with $O_2$ ref = 15% | SFV = 840 $Nm^3/GJ$ |
| Stationary gas turbines burning natural gas with $O_2$ ref = 15% | SFV = 810 $Nm^3/GJ$ |

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 $Nm^3/GJ$.

**Calculating emission factors from given concentrations** (VGB/EURELECTRIC 2010)**:**

EF = C x SFV/1,000

| | |
|---|---|
| EF: | Emission factor (g/GJ) |
| C: | Concentration in the dry flue gas at reference oxygen content ($mg/Nm^3$) |

# 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$^3$; 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$^3$ (at 10% $O_2$). The comparatively high concentration of 400 pg I-TEQ/Nm$^3$ (at 10% $O_2$) 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/m³, Dutch measurements gave 0.07 ng I-TEQ/m³ (LUA 1997). A recent study from Belgium reported PCDD/PCDF concentrations below 0.1 g I-TEQ/Nm³ (at 5% $O_2$) 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, ∑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 (µg TEQ/TJ)** | | | | |
|---|---|---|---|---|---|---|
| | **Classification** | **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 Σ6PCB emission factors for source category 3d Household Heating and Cooking with Biomass**

| **3d** | **Household Heating and Cooking with Biomass** | **Emission Factors (mg/TJ)** |
|---|---|---|

| | 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)** | | | | |
|---|---|---|---|---|---|---|
| | **Classification** | **Air** | **Water** | **Land** | **Product** | **Residue ng/kg** |
| 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/m³. An average value of 0.05 ng TEQ/m³ was chosen for natural gas. Based on an average heating value of 32–35 MJ/m³ 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 m³ 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/m³; 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/m³, 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/Nm³ and as low as 0.0001 ng TEQ/Nm³; the means were 0.0105 ng TEQ/m³ and 0.0008 ng TEQ/m³ for the normal operation conditions and 0.003 ng TEQ/Nm³ and 0.0002 ng TEQ/Nm³ 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/Nm³. 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/Nm³, temperatures over 300°C increase the likelihood of finding higher emissions, typical concentrations would be 0.3 ng TEQ/Nm³ 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 n the years between 1989 and 1993) showed measured concentrations between 4.1 and 42 ng N-TEQ/Nm³. 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/Nm³. Measurements at two annular shaft kilns in Germany were all below 0.05 ng TEQ/Nm³. 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/Nm³. 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 | Emission Factors (µg TEQ/t brick produced) | | | | |
|---|---|---|---|---|---|---|
| | **Classification** | **Air** | **Water** | **Land** | **Product** | **Residues*** |
| 1 | No emission abatement in place and using contaminated fuels | 0.015 | - | NA | 0.01[i] | 0.001[iii] |
| 2 | No emission abatement in place and using non-contaminated fuels | 0.001 | - | NA | 0.001[ii] | 0.0001[iv] |
| | 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

[i] Derived from field measurements at Mexican artisanal brick kilns using waste oil

[ii] Derived from coal and virgin wood fired brick kilns in Mexico, South Africa at industrial and artisanal scale

[iii] Derived from Mexican artisanal brick kilns fired with contaminated fuels

[iv] 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 | Emission Factors (mg/t brick produced) | | | | |
|---|---|---|---|---|---|---|
| | **Classification** | **Air** | **Water** | **Land** | **Product** | **Residues*** |
| 1 | No emission abatement in place and using contaminated fuels | 225 | - | NA | 100[i] | 1[iii] |
| 2 | No emission abatement in place and using | 32 | - | NA | 20[ii] | 0.1[iv] |

| | | | | | | |
|---|---|---|---|---|---|---|
| | 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

[i] Derived from field measurements at Mexican artisanal brick kilns using waste oil

[ii] Derived from coal and virgin wood fired brick kilns in Mexico, South Africa at industrial and artisanal scale

[iii] Derived from Mexican artisanal brick kilns fired with contaminated fuels

[iv] 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/m³ (at 6% $O_2$) and 0.23-4.2 pg TEQ/m³ (at 6% $O_2$). 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 $10^{-3}$ and 0.25 $10^{3}$ µg 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 µg TEQ/t of fuel burned. Thus, an emission factor to air of 0.001 µg TEQ/t of fuel burned is specified for class 3. Based on these results, an emission factor for ethanol- powered vehicles of 0.0007 µg 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/m³ 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** | | | | |
|---|---|---|---|---|---|---|
| | **Classification** | **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)** | | | | |
|---|---|---|---|---|---|---|
| | **Classification** | **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/Nm³ (at 11% $O_2$) 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/m³ and a maximum of 0.3 ng TEQ/m³ 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/m³ (= 4.25 µg TEQ/t) and the median was 0.17 ng TEQ/m³ (= 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$^{nd}$ 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)** | | | | |
|---|---|---|---|---|---|---|
| | **Classification** | **Air** | **Water** | **Land** | **Product** | **Residue** |
| 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 µg TEQ/t of straw burned and, the $EF_{Air}$ for rice straw was 0.537 µg 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 µg TEQ/t of fuel (range 98-148 µg TEQ/t of fuel) (Hawaii) and 12 µg TEQ/t of fuel (range 5.5 -26 µg TEQ/t of fuel) (Florida 1) and 5 µg TEQ/t of fuel (range 0.13-1.72 µg 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) µg TEQ/t of fuel consumed for the in-field, over a brick hearth, and burn facility experiments, respectively. In Australia, an $EF_{Alir}$ 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 an laboratory burn facility were used to estimate PCDD/PCDF emission factors of 19 µg TEQ/t of fuel (range 1-56 µg 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 µg TEQ/t of fuel to 13 µg 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) µg 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 µg TEQ/t for sugar cane and 0.15 µg 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 2nd 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 | Emission Factors (µg TEQ/t material burned) | | | | |
|---|---|---|---|---|---|---|
| | **Classification** | **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 (µg 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 $EF_{Air}$. For order-of-magnitude assessments, the earlier $EF_{Air}$ was changed to 100 µg 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 (1st and 2nd 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 μg TEQ/t $C_{burned}$ to 14,000 μg TEQ/t $C_{burned}$.[20] 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 μg TEQ/t $C_{burned}$ to 14,000 μg 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 $CO/CO_2$; 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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[20] $C_{burned}$ is calculated from the carbon content of CO and $CO_2$ 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 µg 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 µg TEQ/t of PVC or 51 µg TEQ/t of the wood/PVC mixture is obtained. Further it was assumed that deposited soot is additional to this a further 2,200 µg TEQ/t PVC or 200 µg TEQ/t PVC/wood mixture was produced. Ikeguchi and Tanaka (1999) provide air emission factors for the open burning of various wastes (220 µg TEQ/t for scrap tires, 1,000 µg TEQ/t for electric wire tube and 6,600 µg TEQ/t for agricultural plastics (PVC)). Testing in Denmark of PCDD/PCDF released from burning chemicals (Vikelsoe and Johansen 2000) showed an enormous range of air emission factors (at 500°C) from 1 µg TEQ/t for dichlobenil, up to 740,000 µg TEQ/t for pentachlorophenol (PCP), and 100 µg 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 µg TEQ/t to air, 83 µg TEQ/t in locally deposited soot and for industrial fires 500 µg TEQ/t to air and 500 µg 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 µg 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 µg TEQ for the old car, 44 TEQ µg for the new car, 2,000 µg TEQ for the subway car and 9,200 µg 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 µg 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 $CO_2$ 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 (µg 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 *et al.* 2011 |
| 660 | 152 | 277 | Soloarzano Ochoa *et al.* 2011 |
| 290 | 67 | 122 | Solorzano Ochoa *et al.* 2011 |
| 870 | 200 | 365 | Solorzano Ochoa *et al.* 2011 |
| 950 | 219 | 399 | Solorzano Ochoa *et al.* 2011 |
| 950 | 219 | 399 | Solorzano Ochoa *et al.* 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).

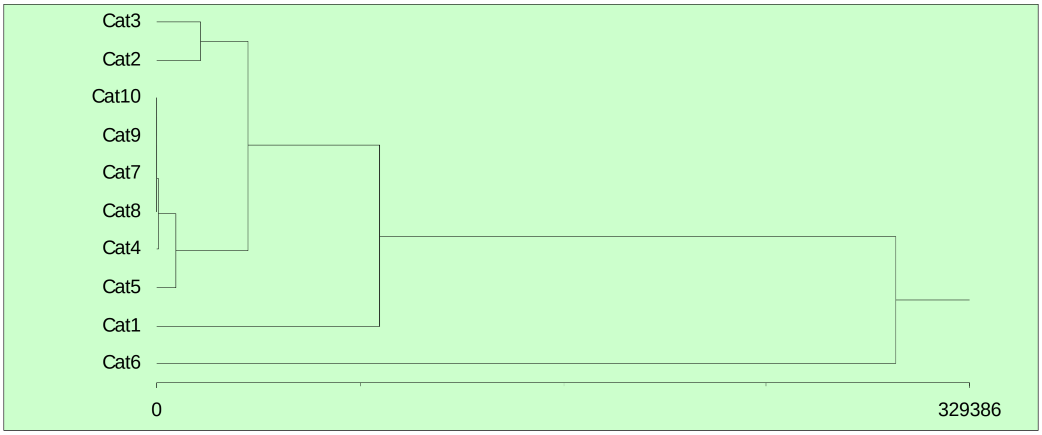

**Figure III.46.1 Dendrogram of the ten source groups in the UNEP Toolkit applied to 60 PCDD/PCDF inventories demonstrating similarities and dissimilarities**

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** | |
|---|---|---|---|---|
| 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% |
| 25th Percentile | 1% | 0% | 1% | 0% |
| 75th 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 | $EF_{Air}$ (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 x $10^{-5}$ 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** | **$EF_{Air}$ (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 *et al*. (2008) (Japan) | 0.006/t pulp |

In Japan, power boilers burning black liquor have an $EF_{Air}$ of 0.006 µg/t of pulp for PCDD/PCDF and dioxin-like PCBs, an $EF_{Air}$ of 2.4 µg/t for HCB and an $EF_{Air}$ 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 $m^3$/ADt pulp and an unbleached Kraft mill has a water discharge rate of 15-25 $m^3$/ADt pulp. For sulfite mills, water usage is about 70 $m^3$/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-$Cl_4$DD and 2,3,7,8-$Cl_4$DF in pulp mill effluents. The results showed that 2,3,7,8-Cl4DD was not detected in any sample above the proposed guideline concentration of 10 pg/L. 2,3,7,8-Cl4DF 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 $m^3$/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 $Cl_2$ in bleaching processes. Replacing $Cl_2$ with chlorine dioxide ($ClO_2$) – so-called elemental chlorine free (ECF bleaching) – may reduce 2,3,7,8-$Cl_4$DD and 2,3,7,8-$Cl_4$DF concentrations to non-detectable levels. However, $ClO_2$ commonly contains small amounts of $Cl_2$ so that PCDD/PCDF formation may still occur during ECF bleaching. The extent of such formation depends on the amount of $Cl_2$ in the $ClO_2$ and on the quantity of lignin remaining in the pulp (commonly expressed in "kappa numbers"). With high kappa numbers and more $Cl_2$ in the $ClO_2$, 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-$Cl_4$DF = 13.6 ng/kg and 2,3,7,8-$Cl_4$DD = 2.0 ng/kg but high concentrations of 1,2,3,7,8-$Cl_5$DD = 29.8 ng/kg and Cl6DD = 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-$Cl_4$DD, 1,2,3,7,8-$Cl_5$DD, and 1,2,3,4,7,8-$Cl_6$DD but had no quantifiable 2,3,7,8-substituted $Cl_4$DF and $Cl_5$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 $Cl_2$ in the first bleaching stage by $ClO_2$ will dramatically reduce the formation of 2,3,7,8-$Cl_4$DD and 2,3,7,8-$Cl_4$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 ($Cl_2$ 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 $EF_{Product}$ of 1 µg TEQ/t paper. Applying new technology will lower the emission factor to 0.1 µg TEQ/t.

Unbleached papers have an emission factor of 0.5 µg TEQ/t.

Recycling papers will have an emission factor of either 10 µg TEQ/t for recycling papers originating from pulp made by the old Kraft process or 3 µg 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[21], green liquor dregs[22], 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 µg 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 µg 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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[21] lime mud that pebbled in the kiln but did not calcine, from chemicals used in kraft pulp mills.

[22] 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 $Cl_4DD$ and $Cl_4DF$ 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 $EF_{Residue}$ 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 $EF_{Residue}$ 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<br>(0.35) | 1.2-1.6<br>(1.4) | 6.3-18.9<br>(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 $EF_{Residue}$ of 228 µg 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.

**$EF_{Air}$:** An $EF_{Air}$ of ND is proposed for stand-alone chlor-alkali facilities.

**$EF_{Water}$:** An $EF_{Water}$ 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, $EF_{Water}$ 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 $EF_{Water}$ of 17 µg TEQ/ECU is recommended for Class 2a, approximately 10-fold higher than Class 2b.

**$EF_{Product}$:** Data describing PCDD/PCDF concentrations in $Cl_2$ or its co-products, $H_2$ and NaOH, are not available, and an $EF_{Product}$ of ND is recommended.

**$EF_{Residue}$:** 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 $EF_{Residue}$ 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[23], 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*.

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[23] 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 $EF_{Residue}$ 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 $EF_{Residue}$ 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 ($FeCl_3$) 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$^3$) | | PCDD/PCDF Emissions (µg/t PVC) | |
|---|---|---|---|
| **Vinyl Institute (2002) at 7% $O_2$** | **Eastern Research Group (2011) at 3% $O_2$** | **Eastern Research Group Baseline (2011)$^A$** | **Eastern Research Group after new emission limit$^B$ is in place (2011)$^C$** |
| **Range;<br>Average (Median)** | **Range;<br>Average (Median)** | **Range;<br>Average (Median)** | **Range;<br>Average (Median)** |
| 0.0014-0.042;<br>0.013 (0.01) | 0.0017-0.91; 0.08 (0.017) | 0.000053-0.026;<br>0.005 (0.00061) | 0.000053-0.020; 0.0023 (0.00050) |

[A] 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$^4$ 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%.

[B] 0.023 ng TEQ/Nm$^3$at 3% $O_2$.

[C] 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$^3$). 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. |
|---|---|

| | **(ng I-TEQ/m$^3$)** | | | |
|---|---|---|---|---|
| | **Vinyl Institute (2002) at 7% $O_2$** | | **Carroll Jr. *et al*. (2001) at 7% $O_2$** | |
| | **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 ECVM charter met the charter commitment of 0.1 ng TEQ/Nm$^3$ 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 $10^{-8}$ mg TEQ/kg VCM (0.042 µg TEQ/t VCM produced).[24]

### 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.

### $EF_{Air}$ for Vent and Liquid/Vent Combustors or Thermal Oxidizers at EDC, EDC/VCM or EDC/VCM/PVC facilities

Either the suggested $EF_{Air}$ may be chosen, or an $EF_{Air}$ may be calculated by multiplying PCDD/PCDF concentration in the flue gas by flue gas flow rates, in m$^3$/hour, and hours per year of operation.

- Class 1: an $EF_{Air}$ of 5 µg TEQ/t VCM based on Carroll *et al*. (2001) or a flue gas concentration of 5 ng TEQ/Nm$^3$ is used, a factor of 10 higher than Class 2.
- Class 2: an $EF_{Air}$ of 0.5 µg TEQ/t VCM or a flue gas concentration of 0.5 ng TEQ/Nm$^3$ is used, a factor of 10 higher than Class 3.
- Class 3: an $EF_{Air}$ of 0.05 µg/t VCM or a flue gas concentration of 0.1 ng TEQ/Nm$^3$ is used based on EU BREF (EU IPPC 2003).

### $EF_{Air}$ for PVC-only facilities

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[24] 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 µg TEQ/ton PVC or PCDD/PCDF concentration of 1 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 µg TEQ/ton PVC or emission concentration limit of 0.1 ng TEQ/$Nm^3$, a factor of 5 larger than Class 3.
- Class 3: PCDD/PCDF emission of 0.021 µg 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 ng TEQ/$Nm^3$ (Eastern Research Group 2011, CMAI 2011b).

For VCM production, air emission factors for HCB and PCBs of 72 µg/t and 8.9 µg/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 ng TEQ/L in effluent (EU IPPCB 2003). OSPARCOM and the ECVM charter (EU BREF section 12.4.7) cite 1 µg 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 pg I-TEQ/L, with an average of 4.7 pg I-TEQ/L (ND = DL/2; congeners detected in all samples), and emission factors of 0.0032 to 0.032 µg I-TEQ/t EDC, with an average of 0.015 µg I-TEQ/t EDC; and
- For PVC only facilities, concentrations in wastewater of 0.0 to 2.0 pg I-TEQ/L, with an average of 0.43 pg I-TEQ/L (ND = 0; 4 of 6 samples with no detected congeners), and emission factors of 0.0 to 0.04 µg I-TEQ/t PVC , with a average of 0.0083 µg 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 pg I-TEQ/L, with a median of 55.2 pg I-TEQ/L; and
- For EDC, VCM, and other organic operations, concentrations of 3.12 to 174 pg I-TEQ/L, with a median of 34.3 pg I-TEQ/L; and

- PVC-only operations, one facility, 0.333 pg 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[25], 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).

**$EF_{Water}$ for EDC/VCM/PVC and EDC/VCM facilities:**

- Class 1: an $EF_{Water}$ 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 $EF_{Water}$ 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 $EF_{Water}$ 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.

**$EF_{Water}$ for Suspension and Dispersion/Emulsion PVC-only facilities:**

- Class 1: an $EF_{Water}$ 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 $EF_{Water}$ of 0.003 µg TEQ/t PVC is presented, based on the average $EF_{Water}$ 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 $EF_{Water}$ 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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[25] 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 µg TEQ/t EDC capacity. The average of these two emission factors is 0.08 µg TEQ/t EDC capacity.

**$EF_{Land}$ for wastewater treatment sludge from EDC/VCM/PVC facilities:** An $EF_{Land}$ of 0.08 µg TEQ/t EDC capacity (0.01 µg 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 pg 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.

**$EF_{Product}$ 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 ng/t level; however, due to that extremely dilute concentration (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 $EF_{Product}$ for VCM.

**$EF_{Product}$ 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:

**$EF_{Product}$ for EDC produced via oxychlorination or mixed oxychlorination/direct chlorination:**

- For Class 1: an $EF_{Product}$ of 2.0 µg TEQ/t EDC is presented, a factor of 10 greater than Class 2.
- For Class 2: an $EF_{Product}$ 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 $EF_{Product}$ 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).

**$EF_{Product}$ 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).[26] 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)[A] | 0.023[B] | 0.077[B] |
| EDC/VCM, and EDC/VCM/PVC: Fixed bed oxychlorination reactors | 93-12,000[C] | 2200 (310)[C] | 0.37 | 1.5 |
| EDC/VCM, and EDC/VCM/PVC Fluidized bed oxychlorination reactors | | | 3.9 | 7.9 |

[A] Two samples only

[B] per ton PVC

[C] 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:

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[26] 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 μg I-TEQ/t, I-TEQ (median 15,000, average 29,000 μg I-TEQ/t spent catalyst) and derived $EF_{Residue}$ ranging from 0.018 to 8.1 μg 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 μg I-TEQ/t EDC from fixed bed facilities and 0.045 μg 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***

**$EF_{Residue}$ for EDC/VCM facilities for wastewater treatment solids:**

- For Class 1: an $EF_{Residue}$ of 0.75 µg TEQ/t EDC produced via fixed bed oxychlorination or 4 µg 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 $EF_{Residue}$ of 0.2 µg TEQ/t EDC from sites with fixed bed oxychlorination or 2 µg 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: $EF_{Residue}$ of NA is accorded to facilities that incinerate wastewater treatment solids; for those that do not, 0.095 µg TEQ/t EDC from sites with fixed bed oxychlorination and 0.4 µg 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).

**$EF_{Residue}$ for PVC-only facilities, wastewater treatment solids:**

- For Class 1: an $EF_{Residue}$ of 0.095 µg TEQ/t PVC is based on the highest value derived by the Vinyl Institute (2002).
- For Class 2: an $EF_{Residue}$ of 0.06 µg TEQ/t PVC is based on the average of the values derived by the Vinyl Institute (2002).
- For Class 3: an $EF_{Residue}$ of NA is presented for facilities that incinerate waste water treatment solids or 0.005 µg TEQ/t PVC for those that do not is presented, based on the lowest value derived by the Vinyl Institute (2002).

**$\text{EF}_{\text{Residue}}$ for EDC/VCM facilities with fixed-bed oxychlorination, as spent catalyst:**

- Class 1: an $\text{EF}_{\text{Residue}}$ of 8 µg I-TEQ/t EDC based on the highest value derived by the Vinyl Institute.
- Class 2: an $\text{EF}_{\text{Residue}}$ of 0.85 µg I-TEQ/t EDC is the average of the values derived by the Vinyl Institute.
- Class 3: an $\text{EF}_{\text{Residue}}$ 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**

**$\text{EF}_{\text{Residue}}$ for maintenance waste sent to landfill from EDC/VCM facilities:**

- In lieu of an $\text{EF}_{\text{Residue}}$, 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[A] | | | | µg TEQ/t Product | | |
|---|---|---|---|---|---|---|---|---|
| | | | WWTS[B] | | | | | |
| | Liquid and Liquid/Vent Combustors | Treated Waste water | Fixed Bed | Fluid-ized Bed | Spent Catalyst, Fixed Bed Oxychlorination | EDC[C] | 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[D] | 0.006 | NA | NA |

[A] Assumes a balanced or nearly balanced direct chlorination-oxychlorination process. Sites operating direct chlorination only are ND.

[B] Wastewater Treatment Solids.

[C] 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.

[D] 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:

**$EF_{Product}$**: 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 $EF_{Product}$ 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 $EF_{Air}$ and $EF_{Water}$.

**$EF_{Product}$:** For PCP, an $EF_{Product}$ of 634,000 μg TEQ/t is presented, based on Tondeur *et al*. (2010).

**$EF_{Product}$:** For PCP-Na, an $EF_{Product}$ of 12,500 μg TEQ/t is presented, based on data from the Republic of China (2007).

Further, Bao *et al.* (1994) calculate an $EF_{Residue}$ 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 was 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:

**$\mathbf{EF_{Product}}$:** For 2,4,5-trichlorophenoxyacetic acid, an $EF_{Product}$ of 7,000 µg TEQ/t is presented (EC 1999b, NATO/CCMS 1992).

**$\mathbf{EF_{Product}}$:** For 2,4,6-trichlorophenol, an $EF_{Product}$ 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.

**$\mathbf{EF_{Product}}$:** For CNP produced using old technologies, an $EF_{Product}$ of 9,200,000 µg TEQ/ton is presented, based on the concentrations reported for the two oldest samples analyzed by Masunaga (1999).

**$\mathbf{EF_{Product}}$:** For CNP produced using new technologies, an $EF_{Product}$ 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) | | | | |
|---|---|---|---|---|---|---|
| | Classification | Air | Water | Land | Product | Residue |
| 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:

**$EF_{Product}$ 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 **$EF_{Land}$**.

**$EF_{Product}$ 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 **$EF_{Land}$**.

### 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 *et al*. (1981) |
| | 6,800 of 2,3,7,8-TCDD | Germany | Hagenmaier (1986) |
| | 4,800 | Germany | Wilken *et al*. (1992) |
| | 0–16 | Japan | Masunaga *et al*. (2001) |
| | 0.12-1.8 | Australia | Holt *et al*. (2010) |
| | 160-180 | | |
| | ~300* (est.)*** | U.S. | Gullett *et al*. (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 *et al*. (1992) |
| | 160 | Russia | Schecter *et al*. (1993) |
| 2,4-D dimethylamine, 46.9% | 8.7* | U.S. | Huwe *et al*. (2003) |
| 2,4-D isooctyl ester, 61.7% | 731* | U.S. | Huwe *et al*. (2003) |
| 2,4-D isooctyl ester, 66.2% | 2,627* | U.S. | Huwe *et al*. (2003) |
| 2,4-D isooctyl ester, 67.2% | 27.7* | U.S. | Huwe *et al*. (2003) |
| 2,4-D isooctyl ester, 88.8% | 1,379* | U.S. | Huwe *et al*. (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. | Schecter (1998) |
| 2,4-D Herbicides purchased in Palestine and Israel | 96.4*<br>828* | Palestine and Israel | Schecter (1998) |
| 2,4-D Herbicide, Chimprom, Ufa, Russia | 142* | Russia | Schecter (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, Gullet *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 ΣTCDF 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 ΣTCDF 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.

**$EF_{Product}$ for PCDD/PCDF:** 0.12 µg 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 µg 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 µg 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) | | | | |
|---|---|---|---|---|---|---|
| **Classification** | | **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) | | | | |
|---|---|---|---|---|---|---|
| **Classification** | | **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:

**$EF_{Product}$ 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.

**$EF_{Product}$ 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.

**$EF_{Product}$ 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 choranil 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 $EF_{Product}$ for chloranil. Total PCB levels in the three chloranil samples ranged from 1,179.4 to12,413.7 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:

**$EF_{Product}$:** For minimal purification of chloranil, an $EF_{Product}$ of 1,500,000 μg TEQ/t is presented.

**$EF_{Product}$:** For moderate purification of chloranil, an $EF_{Product}$ of 26,000 μg TEQ/t is presented.

**$EF_{Product}$:** For high purification of chloranil, an $EF_{Product}$ of 150 μg TEQ/t is presented.

An $\mathbf{EF_{Product}}$ of 400,000 µg 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) | | | | |
|---|---|---|---|---|---|---|
| | **Classification** | **Air** | **Water** | **Land** | **Product** | **Residue** |
| 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:

$\mathbf{EF_{Product}}$ for phthalocyanine copper: 0.07 µg TEQ/kg; and

$\mathbf{EF_{Product}}$ for phthalocyanine green: 1.4 µg 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) | | | | |
|---|---|---|---|---|---|---|
| | **Classification** | **Air** | **Water** | **Land** | **Product** | **Residue** |
| 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:

**$EF_{Product}$** for Blue 106: 35 µg TEQ/kg;

**$EF_{Product}$** for Blue 108: 0.1 µg TEQ/kg; and

**$EF_{Product}$** 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.

$\mathbf{EF_{Product}}$ using low-end production technologies: 1700 µg TEQ/t, based on the highest value from Menoutis and Parisi (2002).

$\mathbf{EF_{Product}}$ using mid-level production technologies: 60 µg TEQ/t of product, based on the five lowest values from Menoutis and Parisi (2002).

$\mathbf{EF_{Product}}$ 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 ($TiCl_4$) and Titanium Dioxide ($TiO_2$)

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% $TiO_2$, and ilmenite, which may contain between 44% and 70% $TiO_2$ – into $TiCl_4$. This conversion is carried out in a fluidized bed chlorinator in the presence of $Cl_2$ at a temperature of approximately 900°C, with the addition of petroleum coke as a reductant. The volatile $TiCl_4$, 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. $TiCl_4$ 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 $TiCl_4$ is then oxidized to produce $TiO_2$ and $Cl_2$ that is driven off is recycled to the chlorinator. The pure $TiO_2$ 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 $TiO_2$. 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 $TiO_2$ 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 $TiCl_4$/$TiO_2$ 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 µg TEQ/t of product were representative.

PCDD/PCDF concentrations in residues from $TiCl_4/TiO_2$ 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 µg TEQ/t of product (USEPA 2010b).

In the U.S., a $TiCl_4/TiO_2$ 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 $EF_{Air}$ for PCDD/PCDF releases from $TiCl_4/TiO_2$ production.

**$EF_{Water}$:** Values range from .0012 to .1771 µg TEQ/t of product based on 2010 TRI data reported by USEPA and production data from TZ Minerals International.

**$EF_{Product}$:** ND.

**$EF_{Resdiue}$:** Based on 2010 TRI data reported by USEPA and production data from TZ Minerals International current solid residues range from 8 to 42 µg TEQ/t of product.

### Caprolactam (2-Azacycloheptanone)

For PCDD/PCDF, an $EF_{Air}$ of 0.00035 µg I-TEQ/t of caprolactam and, for HCB and PCB, $EF_{Air}$ of 3.2 and 8.1 µg 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 $EF_{Water}$ 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 $EF_{Water}$ 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.

**$EF_{Air}$:** An $EF_{Air}$ 0.00035 µg TEQ/t of caprolactam has been derived by Iwata *et al*. (2008).

**$EF_{Water}$:** In lieu of an $EF_{Water}$, 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 µg TEQ/t of caprolactam and PCB air emission factor of 8.1 µg 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).[27] 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$^3$ (Jansson 1999). The California Air Resources Board (1999) determined an EF$_{Air}$ 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$_{Air}$ 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$_{Air}$ of 56.2 ng TEQ/barrel (353.5 ng/m$^3$ oil).

For flares at Danish refineries, Henricksen *et al*. (2006) derived an EF$_{Air}$ of 0.25 μg TEQ/TJ of fuel.

**EF$_{Air}$** of 2.28 ng TEQ/barrel (0.0143 μg TEQ/m$^3$ oil; 0.0168 μg TEQ/t oil)[28] 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$_{Air}$** of 56.2 ng TEQ/barrel (0.353 μg TEQ/m$^3$ oil; 0.413 μg TEQ/t oil) for refinery coking units, based on the value derived by RTI (2011).

**EF$_{Air}$** of 0.25 μg TEQ/TJ of fuel for flares at oil refineries, based on value presented by Henricksen *et al.* (2006).

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[27] Petroleum Online. Overview. http://www.petroleumonline.com/content/overview.asp?mod=8

[28] 1 barrel of oil = 0.159 m$^3$ 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.

**$EF_{Water}$** 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.

**$EF_{Residue}$** 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 ± 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 $Sb_20_3$/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/$m^3$. 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 dying 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 ($Cl_7$ and $Cl_8$), 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).

**$EF_{Product}$** of 100 μg TEQ/t is presented as a reasonable upper limit value, based on values reported in existing studies.

**$EF_{Product}$** of 0.1μg TEQ/t is presented as a reasonable lower limit value, based on values reported in existing studies.

**$EF_{Product}$** 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 $EF_{Residue}$. 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$^3$ 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.

**$EF_{Product}$** of 1,000 μg TEQ/t is presented as a reasonable upper limit value, based on values reported in existing studies.

**$EF_{Product}$** 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 8eTobacco 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/Nm³ to 3.51 ng I-TEQ/Nm³ with a median of 0.16 ng I-TEQ/Nm³ (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/Nm³ 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 $EF_{AIR}$ of 10 µg TEQ/body cremated. However, PCDD/PCDF concentrations at the stack ranged from 10.5 to 28.6 ng I-TEQ/m³ with an average of 17.6 ng I-TEQ/m³ (at 11% $O_2$). The $EF_{AIR}$ 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$^3$. However, a high concentration of 4.18 ng I-TEQ/m$^3$ 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$^3$).

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$^3$/h of flue gas and produces about 50 kg product per hour. The flue gas volume will be 6,000 m$^3$/t product. With the measured data of 1.02 ng TEQ/m$^3$ for a smoke house without thermal afterburning and 0.1 ng TEQ/m$^3$ 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 $EF_{Residue}$ of 0.1 µg TEQ/million cigarettes is presented based on Aoyama *et al*. (2003).

An $EF_{Residue}$ of 0.3 µg 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 m³ 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/$m^3$ 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 µ TEQ/t waste for landfills which contains industrial wastes from category 1 to 8, class 2 with an emission factor of 0.5 µg TEQ/t for landfills which may contain hazardous wastes and class 3, with an emission factor of 0.05 µg 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[29] 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 consistutes 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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[29] 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 $EF_{Product}$ will be used for the $EF_{Land}$.

### 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 m³) 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 $EF_{Product}$ is the $EF_{Land}$.

### 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 $EF_{Product}$ of 5 ng TEQ/kg d.w. should be applied for compost produced from clean organics (separated at source) or green waste.

An $EF_{Product}$ 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[30].

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[30] Organic residues from industrial processes with known relevant PCDD/PCDF emissions should not be used for composting purposes.