PART II DEFAULT EMISSION FACTORS

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

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

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

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

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

1 – Waste Incineration

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

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

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

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

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

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

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

1a Municipal Solid Waste Incinerators

Municipal solid waste (MSW) is defined differently among countries as well as among international agreements. MSW typically includes almost any solid waste generated by households during normal daily life and it also commonly includes wastes produced in industrial, commercial and agricultural activities. Common constituents in MSW include paper and cardboard, plastics, food and kitchen residues, cloth and leather, wood, glass, and metals as well as dirt and rocks and other inert materials. Small quantities of hazardous materials such as batteries, paints, drugs, and some household chemicals also occur in MSW. Nonetheless, most authorities consider MSW as non-hazardous.

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

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

Emission Factors

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

Guidance for Classification of Sources

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

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

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

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

Class 4 is limited to state-of-the-art MSW incinerators equipped with sophisticated APC technologies, such as activated carbon adsorption units or SCR DeDiox$^{@}$ systems that should be capable of ensuring compliance with a strictly enforced regulatory value for air emissions in flue gases that is equivalent to 0.1 ng TEQ/Nm^3 at 11% O_2).

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

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

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[7] The term "fly ash" is used here to include dust from boiler and dedusting, residues from flue gas cleaning without filter dust, residues from flue gas cleaning and filter dust.
[8] The term "bottom ash" is used here also to include slag.

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

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

Activity rates

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

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

Level of Confidence

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

1b Hazardous Waste Incinerators

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

The term "hazardous waste" as used in the Toolkit does not include medical waste since hazardous and medical wastes have different origins and the technologies for their treatment are different (see source category 1c Medical Waste Incinerators). Typically HW incinerators are special technology incinerators or rotary kiln type furnaces. Special technology incinerators include very low technology grate, or muffle furnaces. Since the classification of hazardous waste is highly dependent on country-specific legislation and on the number of different technologies used for hazardous waste, incineration plants can have many features. A detailed discussion of hazardous waste incineration technologies can be found in the BAT&BEP Guidelines.

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

Emission Factors

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

Guidance for Classification of Sources

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

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

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

Class 3 incinerators have further improved combustion efficiencies and more efficient systems resulting in PCDD/PCDF concentrations of about 1 ng TEQ/Nm^3 (at 11% O_2). Also, the specific flue gas volume flow rate is reduced to 10,000 Nm^3/t HW.

Class 4 is limited to highly sophisticated hazardous waste incineration plants that are capable of complying with a regulatory value of 0.1 ng TEQ/Nm^3 (at 11% O_2), such as legislated in the in European Union. Class 4 represents the current state-of-the-art in HW incineration and APC technology with stack gas flow rates of some 7,500 Nm^3/t HW.

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

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

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

Activity rates

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

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

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

Level of Confidence

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

1c Medical Waste Incinerators

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

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

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

Emission Factors

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

Guidance for Classification of Sources

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

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

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

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

Class 4 includes highly sophisticated medical waste incineration plants that are capable of complying with an air emission 0.1 ng TEQ/Nm³ (at 11% O_2). Whether these plants are continuous or batch type operations is not relevant when they are preheated with oil or natural gas to achieve a furnace operating temperature of usually well above 900°C or higher before medical waste is introduced into the furnace.

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

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

* Refers only to bottom ash left in the combustion chamber

** Refers to combined bottom and fly ashes.

Activity rates

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

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

Level of Confidence

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

1d Light-Fraction Shredder Waste Incinerators

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

Emission Factors

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

Guidance for Classification of Sources

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

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

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

Class 3 includes highly sophisticated incineration plants that are capable of achieving a regulatory value for air emissions equivalent to 0.1 ng TEQ/Nm³ (at 11% O_2).

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

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

Activity rates

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

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

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

Level of Confidence

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

1e Sewage Sludge Incinerators

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

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

Emission Factors

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

Guidance for Classification of Sources

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

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

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

Class 3 includes modern state-of-the-art facilities, continuous-feed fluidized bed incinerators with optimized APC systems capable of consistently meeting the emission limits equivalent to 0.1 ng TEQ/Nm^3 (at 11% O_2)

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

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

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

Activity rates

Activity rates for sewage sludge incineration may be available from:

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

Level of Confidence

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

1f Waste Wood and Waste Biomass Incinerators

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

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

Emission Factors

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

Guidance for Classification of Sources

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

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

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

Class 3 includes modern, continuously-fed and controlled, state-of-the-art facilities, equipped with full APC systems capable of meeting emission limits equivalent to 0.1 ng TEQ/Nm^3 (at 11% O_2).

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

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

Activity rates

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

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

Level of Confidence

The default emission factors for all three classes were determined based on reported concentrations from a number of studies in Europe and North America. Measured data for bottom ash could not be obtained; consequently the default emission factors for residue only consider fly ash. The data presented in these different studies are in agreement, and the emission factors are assigned a medium confidence level.

1g Destruction of Animal Carcasses

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

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

Emission Factors

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

Guidance for Classification of Sources

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

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

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

Class 3 includes modern state-of-the-art, continuously-fed and controlled facilities with full APC systems capable of meeting emission limits equivalent to 0.1 ng TEQ/Nm^3 (at 11% O_2).

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

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

Activity rates

Activity rates for animal carcass incineration may be available from

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

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

Level of Confidence

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

2 – Ferrous and Non-Ferrous Metal Production

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

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

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

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

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

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

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

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

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

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

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

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

2a Iron Ore Sintering

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

The waste gas flow from a sinter plant varies from 350,000 to 1,600,000 Nm³/hour, depending on the plant size and operating conditions. Typically the specific waste gas flow is between 1,500 and 2,500 Nm³/t of sinter (BREF 2012). Waste gases are usually treated by dust removal in a cyclone, electrostatic precipitator, wet scrubber or fabric filter. In plants where high PCDD/PCDF emissions have been identified, high performance scrubbing systems may be installed to reduce emissions, coupled with measures to reduce gas flows.

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

Emission Factors

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

Guidance for classification of sources

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

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

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

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

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

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

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

Activity rates

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

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

Level of Confidence

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

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

2b Coke Production

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

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

Emission Factors

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

Guidance for classification of sources

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

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

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

2b	**Coke Production**	**Emission Factors (µg TEQ/t coke produced)**				
	Classification	**Air**	**Water**	**Land**	**Product**	**Residue**
1	No gas cleaning	3	0.06*	NA	ND	ND
2	APC with afterburner/dust removal	**0.03**	0.06*	NA	ND	ND

* Use factor of 0.006 µg TEQ/t where water treatment is applied.

Activity rates

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

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

Level of Confidence

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

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

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

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

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

Five types of furnaces are commonly used to melt metals in foundries: cupola, electric arc, induction, reverberatory, and crucible. As no information is currently identified regarding foundry processes for die casting of non-ferrous metal alloys, which include induction furnaces, reverberatory or crucible for instance, emission factors of the “iron foundries” section may be used as default factors for such non-ferrous foundry processes.

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

Emission Factors

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

Guidance for classification of sources

In the iron and steel making category:

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

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

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

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

In the iron foundries category:

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

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

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

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

In the hot-dip galvanizing plants category:

Class 1 includes facilities without air pollution control systems;

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

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

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

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

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

* ND where wet scrubbers are used

Activity rates

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

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

Level of Confidence

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

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

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

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

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

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

2d Copper Production

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

Primary copper

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

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

Secondary copper

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

Emission Factors

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

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

Guidance for classification of sources

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

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

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

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

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

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

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

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

Activity rates

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

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

Level of Confidence

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

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

2e Aluminum Production

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

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

Emission Factors

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

Guidance for classification of sources

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

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

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

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

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

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

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

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

Activity rates

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

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

Level of Confidence

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

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

2f Lead Production

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

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

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

Emission Factors

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

Guidance for classification of sources

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

Class 2 Secondary lead production from PVC/Cl_2 free scrap, some air pollution control system.

Class 3 Lead production from PVC/Cl_2 free scrap in highly efficient furnaces, with air pollution control systems including wet scrubbers.

Class 4 Pure primary lead production.

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

2f	**Lead Production**	**Emission Factors (µg TEQ/t lead)**				
	Classification	**Air**	**Water**	**Land**	**Product**	**Residue**
1	Lead production from scrap containing PVC	80	ND	NA	NA	ND
2	Lead production from PVC/Cl_2 free scrap, some APCS	8	ND	NA	NA	50
3	Lead production from PVC/Cl2 free scrap in highly efficient furnaces, with APC including scrubbers	**0.05**	ND	NA	NA	ND
4	Pure primary lead production	**0.4**	NA	NA	NA	ND

Activity rates

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

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

Level of Confidence

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

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

2g Zinc Production

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

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

Emission Factors

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

Guidance for classification of sources

Class 1 Rotary kiln with no air pollution control system.

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

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

Class 4 Zinc melting and primary zinc production.

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

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

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

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

Activity rates

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

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

Level of Confidence

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

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

2h Brass and Bronze Production

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

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

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

Emission Factors

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

Guidance for classification of sources

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

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

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

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

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

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

Activity rates

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

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

Level of Confidence

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

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

2i Magnesium Production

The production of magnesium from ores is largely based on either electrolysis of $MgCl_2$ or chemical reduction of oxidized magnesium compounds. The raw materials used are dolomite, magnesite, carnallite, brines or seawater depending on the process. Magnesium can also be recovered and produced from a variety of magnesium-containing secondary raw materials.

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

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

Emission Factors

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

Guidance for classification of sources

Class 1 Production processes using MgO and coke thermal treatment in Cl2 atmosphere, without treatment of wastewater and with limited gas treatment.

Class 2 Production processes using MgO and coke thermal treatment in Cl2 atmosphere with comprehensive pollution control.

Class 3 Thermal reduction process.

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

2i	**Magnesium Production**	**Emission Factors (µg TEQ/t magnesium)**				
	Classification	**Air**	**Water**	**Land**	**Product**	**Residue**
1	Production using MgO/C thermal treatment in Cl_2 – no treatment on effluent, limited gas treatment	250	9,000	NA	NA	0
2	Production using MgO/C thermal treatment in Cl_2 – comprehensive pollution control	50	30	NA	NA	9,000
3	Thermal reduction process	3	ND	NA	NA	NA

Activity rates

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

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

Level of Confidence

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

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

2j Other Non-ferrous Metal Production

A number of non-ferrous metals are not assigned to a specific category in the Toolkit: cadmium, precious metals, chromium, nickel, ferro-alloys (FeSi, FeMn, SiMn, etc.), alkali metals, etc. A variety of processes are undertaken to produce and refine non-ferrous metals. The exact processes used and the propensity to form PCDD/PCDF are complex and not studied in detail. It is important not to miss potentially significant PCDD/PCDF sources simply because data are insufficient to provide comprehensive emissions factors. Therefore, to provide an initial indication of potential releases, it is suggested that processes in non-ferrous metal production are examined. Releases may occur to air, water, and in residues. When investigating production processes, it is suggested that thermal processes are noted, the type of gas cleaning system applied recorded, and the levels of contamination found in the input materials noted. The use of Cl_2 or hexachloroethane for refining, and the presence of chlorinated compounds in raw materials should also be noted. The Questionnaire provided in the Toolkit will assist in identifying and recording these parameters.

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

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

Emission Factors

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

Guidance for classification of sources

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

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

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

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

Activity rates

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

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

Level of Confidence

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

2k Shredders

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

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

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

Emission Factors

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

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

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

Activity rates

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

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

Level of Confidence

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

2l Thermal Wire Reclamation and E-Waste Recycling

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

Emission Factors

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

Guidance for classification of sources

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

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

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

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

Table II.2.14 PCDD/PCDF emission factors for source category 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	**12,000**	ND	ND	ND	ND
2	Open burning of circuit boards	**100**	ND	ND	ND	ND
3	Basic furnace with afterburner and wet scrubber	40	ND	NA	ND	ND
4	Burning electric motors and brake shoes, etc. – afterburner fitted	3.3	ND	NA	ND	ND

Activity rates

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

Level of Confidence

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

3 – Power Generation and Heating

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

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

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

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

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

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

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

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

3a Fossil Fuel Power Plants

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

Fossil fuel is burned in a wide array of devices for power generation ranging from small stoker fired furnaces to large and highly sophisticated boiler/burner systems with extensive air pollution control plants at the back end. Coal combustion for power generation takes place in two general types of boilers distinguished by the way the ash is extracted from the system. The so-called dry bottom boilers use stokers or pulverized coal burners arranged in an opposed wall, which burn coal in a highly efficient manner leaving the majority of the ash as a dry residue at the bottom of the boiler. The so-called wet bottom boilers use pulverized burners in a cyclone or U-fired arrangement, which leads to much higher combustion temperatures resulting in the ash melting and collected as a liquid slag at the bottom of the boiler. Typical flue gas cleaning devices for large coal-fired power plants consist of units for NOx control (*e.g*. SCR technology), particulate matter control (*e.g*. electrostatic precipitators) and desulphurization (*e.g*. lime stone scrubbing). These devices can reduce PCDD/PCDF emissions as a side effect.

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

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

In some countries such as Australia, Brazil, Canada, China, Estonia, France, Russia, United Kingdom (in Scotland), South Africa, Spain, Sweden, and the USA large quantities of oil shale exist, which can be converted to shale oil, a substance similar to petroleum. In Estonia, for example, more than 90% of the country's electricity is generated from shale oil (Schleicher 2004a). In some countries peat is a domestic energy resource and is used for heat and/or power generation, *e.g*. in Finland or Ireland (McGettigan *et al*. 2009).

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

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

Emission Factors

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

Guidance for classification of sources

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

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

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

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

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

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

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

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

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

* including co-firing of biomass (range: 30-50 µg TEQ/TJ)

** high range depending on fuel quality and combustion conditions (3-100 µg TEQ/TJ)

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

Activity rates

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

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

Level of confidence

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

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

3b Biomass Power Plants

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

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

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

Emission Factors

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

Guidance for classification of sources

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

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

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

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

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

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

*Total of bottom ash and fly ash

** Estimate based on straw combustion, Thailand: Installation with APC (ESP, cyclones, Venturi scrubbers): ca. 20 µg TEQ/TJ

Activity rates

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

Level of confidence

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

3c Landfill Biogas Combustion

Landfill gas and biogas are both generated from anaerobic digestion of organic matter. The resulting gas is a mixture of carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), and ammonia (NH_3), and smaller fractions of combustible gases as well as a large fraction of water (H_2O). The combustible portion of the gas is usually around 50% and the heating value is 15–25 MJ/kg depending on the origin of the gas. The combustion of landfill gas and biogas either occurs in a flare, in gas motors or turbines and other power generating devices.

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

Emission Factors

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

Guidance for classification of sources

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

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

3c	**Landfill Biogas Combustion**	**Emission Factors (µg TEQ/TJ gas burned)**				
	Classification	**Air**	**Water**	**Land**	**Product**	**Residue**
1	Boilers, motors/turbines, flaring	8	ND	NA	NA	NA

Activity rates

This class includes various activities requiring different sources of information:

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

Level of confidence

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

3d Household Heating and Cooking with Biomass

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

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

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

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

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

Emission Factors

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

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

Guidance for classification of sources

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

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

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

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

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

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

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

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

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

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

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

Activity rates

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

Level of confidence

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

3e Household Heating and Cooking with Fossil Fuels

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

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

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

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

Emission Factors

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

Guidance for classification of sources

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

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

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

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

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

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

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

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

*Pandelova *et al*. 2005

Activity rates

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

Level of confidence

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

4 – Mineral Products

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

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

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

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

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

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

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

4a Cement Production

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

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

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

Emission Factors

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

Guidance for classification of sources

Class 1 includes shaft kilns.

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

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

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

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

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

Activity rates

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

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

Level of Confidence

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

4b Lime Production

Lime is used in a wide range of products. Quicklime (or burnt lime) is calcium oxide (CaO) produced by decarbonization of limestone ($CaCO_3$). Slaked lime is quicklime with water content and mainly consists of calcium hydroxide ($Ca(OH)_2$). Major users of lime are the steel industry, construction, pulp and sugar industries.

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

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

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

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

Emission Factors

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

Guidance for classification of sources

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

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

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

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

Activity rates

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

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

Level of Confidence

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

4c Brick Production

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

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

Emission Factors

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

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

Guidance for classification of sources

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

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

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

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

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

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

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

[i] Confirmed/derived with field measurements at Mexican artisanal brick kilns using waste oil

[ii] Confirmed/derived with field measurement at Mexican Kilns using virgin wood

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

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

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

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

Activity rates

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

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

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

Level of Confidence

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

4d Glass Production

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

Emission Factors

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

Guidance for classification of sources

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

Class 2 includes furnaces using dust abatement.

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

4d	**Glass Production**	**Emission Factors (µg TEQ/t product)**				
	Classification	**Air**	**Water**	**Land**	**Product**	**Residue**
1	No dust control or contaminated, poor fuels	0.2	NA	NA	ND	ND
2	Glass production using dust abatement	0.015	NA	NA	ND	ND

Activity rates

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

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

Level of Confidence

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

4e Ceramics Production

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

4f Asphalt Mixing

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

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

Emission Factors

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

Guidance for classification of sources

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

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

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

4f	**Asphalt Mixing**	**Emission Factors (µg TEQ/t asphalt mix)**				
	Classification	**Air**	**Water**	**Land**	**Product**	**Residue**
1	Mixing plant with no gas cleaning, poor fuels	0.07	NA	NA	ND	ND
2	Mixing plant with fabric filter or wet scrubber	0.007	NA	NA	ND	0.06

Activity rates

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

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

Level of Confidence

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

4g Oil Shale Processing

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

The term "oil shale" is a misnomer. It does not contain oil nor is it commonly shale. The organic material is chiefly kerogen and the "shale" is usually a relatively hard rock, called marl. Properly processed, kerogen can be converted into a substance somewhat similar to petroleum. However, oil shale was not converted into "oil" by natural processes and therefore, oil shale has to be heated to a high temperature to become fossil fuel (WEC 2004).

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

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

Emission Factors

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

Guidance for classification of sources

Class 1 includes thermal fractionation process.

Class 2 includes oil shale pyrolisis.

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

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

Activity rates

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

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

Level of Confidence

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

5 – Transport

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

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

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

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

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

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

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

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

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

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

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

5a 4-Stroke Engines

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

Emission Factors

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

Guidance for classification of sources

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

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

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

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

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

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

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

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

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

Activity rates

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

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

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

Level of confidence

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

5b 2-Stroke Engines

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

Emission Factors

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

Guidance for classification of sources

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

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

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

5b	**2-Stroke Engines**	**Emission Factors (µg TEQ/t fuel burned)**				
	Classification	**Air**	**Water**	**Land**	**Product**	**Residue**
1	Leaded fuel*	3.5	NA	NA	NA	NA
2	Unleaded fuel *	2.5	NA	NA	NA	NA

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

Activity rates

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

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

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

Level of confidence

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

5c Diesel Engines

Diesel engines are used in heavy trucks, light trucks, passenger cars, locomotives, heavy construction equipment, boats, Diesel generators, pumps, and farm equipment including tractors and other large equipment. These engines use Diesel (light oil) and a 4-stroke cycle. Compression is used for ignition rather than a spark. Air is taken into the cylinder and compressed. Diesel fuel is added at high pressure and burned, resulting in a more efficient use of fuel and lower emissions. Unfortunately, particle emissions in form of soot are also associated with the operation of Diesel engines, due to incomplete combustion especially during the start-up, warming and load changes. Deposition of this soot can lead to releases via residues. Particulate emissions from Diesel engines are well known to contain high concentrations of polycyclic aromatic hydrocarbons (PAH). However, data on PCDD/PCDF concentrations in Diesel soot are not available. As for other unintentional POPs, no data or almost zero emission for recent diesel engines with after-treatment of emissions have been reported (Laroo *et al*. 2011).

Emission Factors

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

Guidance for classification of sources

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

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

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

5c	**Diesel Engines**	**Emission Factors (µg TEQ/t diesel)**				
	Classification	**Air**	**Water**	**Land**	**Product**	**Residue**
1	Regular Diesel*	0.1	NA	NA	NA	ND
2	Biodiesel	**0.07**	NA	NA	NA	ND

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

Activity rates

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

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

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

Level of confidence

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

5d Heavy Oil Fired Engines

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

Emission Factors

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

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

5d	**Heavy Oil Fired Engines**	**Emission Factors (µg TEQ/t fuel burned)**				
	Classification	**Air**	**Water**	**Land**	**Product**	**Residue**
1	All types	**2**	NA	NA	NA	ND

Activity rates

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

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

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

Level of confidence

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

6 – Open Burning Processes

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

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

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

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

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

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

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

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

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

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

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

6a Biomass Burning

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

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

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

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

Emission Factors

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

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

Guidance for classification of sources

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

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

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

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

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

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

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

Activity rates

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

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

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

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

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

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

Maize	8
Rice	4.4
Sugarcane	5.2

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

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

In the UK, values were derived as follows:

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

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

- Forests/vegetation has been classified according to climatic zones resulting in temperate and Mediterranean (south of France) zones;
- In the temperate zone, forests typically have 20 kg of biomass per square meter (20 kg/m²) corresponding to 200 t/ha. In the Mediterranean zone, the biomass is 4 kg/m² or 40 t/ha;
- In the temperate zone on average, 20% of the vegetation is removed by the fires hence the fuel burned is 40 t/ha. In the Mediterranean zone, the fires are more efficient with an average of 25% above ground biomass removed; thus, the fires in southern France will generate PCDD/PCDF from 10 t of biomass per hectare affected by the fire.

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

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

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

Level of Confidence

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

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

6b Open Burning of Waste and Accidental Fires

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

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

Emission Factors

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

Guidance for classification of sources

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

Class 2 includes accidental fires involving buildings, such as homes and factories. Consequently, emission factors must be given per event and they depend strongly on the materials burned and on the nature of the fire. There is limited information on releases from these fires and a single indicative figure is given to cover all accidental fires excluding fires in vehicles. Chemical fires may lead to very high releases where certain precursor chemicals are involved. However there is insufficient information to assess releases from chemical fires as a distinct category so releases are included in this class of accidental fires. It should be noted that specific incidents may give rise to local contamination and potential “hot spots”.

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

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

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

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

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

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

Level of Confidence

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

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

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

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

7 – Production and Use of Chemicals and Consumer Goods

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

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

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

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

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

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

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

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

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

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

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

Activity Rates

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

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

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

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

7a Pulp and Paper Production

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

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

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

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

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

Emission Factors

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

Guidance for classification of sources

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

Class 1 Recovery boilers fired with black liquor or black liquor/bio-sludge (for sludge for modern bleaching technology)[10];

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

Class 3 Power boilers fired with salt-laden wood.

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

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

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

Class 1 facilities use the Kraft process for pulping non-wood fibers that are potentially contaminated with PCP and bleach with Cl_2.

Class 2 facilities use the Kraft process for pulping fibers that are PCP-free and bleach with Cl_2.

Class 3 facilities use the Kraft process for pulping and bleach first with Cl_2, followed by non-chlorine bleaching technologies.

Class 4 facilities use the sulfite process for pulping and bleach with Cl_2.

Class 5 facilities use the Kraft process for pulping and bleach with chlorine dioxide (ClO_2).

Class 6 facilities use the sulfite process for pulping and bleach with ClO_2 or with totally chlorine-free (TCF) technologies.

Class 7 facilities use thermo-chemical processes to produce pulp and bleach via lignin-saving methods that use sodium dithionite ($Na_2S_2O_3$), peroxide (H_2O_2) or a mixture of these two chemicals.

Class 8 facilities are those engaged in recycling paper from contaminated waste paper – paper that is made from pulp produced by Class 1 through Class 4 facilities.

Class 9 facilities are those engaged in recycling paper from modern paper – paper derived from pulp produced by Class 5 and Class 7 facilities.

To assist in estimating PCDD/PCDF releases, typical PCDD/PCDF values are given in terms of tons of air-dried pulp and paper produced (ADt), with pulp at 90% dryness and paper as the finished paper, which typically has 94-96% dryness. Typical PCDD/PCDF concentrations in effluent, residues and products are also presented for use when mass production data are not available. Emission factors for all wood fiber mills (classes 2-7) are based on the assumption that all such mills have wastewater treatment facilities that produce sludge and effluent low in suspended solids.

Table II.7.3 PCDD/PCDF emission factors for source category 7a Power Boilers in the Pulp and Paper Industry

7a	Pulp and Paper Production	EF_{Air} µg TEQ/ADt[A]	$EF_{Residue}$ µg TEQ/t ash[B]
	Classification		
1	Recovery boilers fueled with black liquor	**0.03**	**ND**
2	Power boilers fueled with sludge and/or biomass/bark	**0.5**	**5**
3	Power boilers fueled with salt-laden wood	**13**	**228**

[A] Air-Dried tons

[B] Bottom ash or bottom ash plus fly ash

Table II.7.4 PCDD/PCDF emission factors for source category 7a Wastewater Effluent from Pulp and Paper Production and Pulp Sludges

7a	Pulp and Paper Production	EF_{Water} Wastewater effluent		$EF_{Residue}$ Sludge	
	Classification	**µg TEQ/ ADt pulp**	**pg TEQ/L**	**µg TEQ/ ADt pulp**	**µg TEQ/t Sludge**

1	Kraft process, Cl_2, non-wood, PCP-contaminated fibers	ND	300*	ND	ND
2	Kraft process, Cl_2	4.5	70	4.5	100
3	Mixed technology (Cl_2 partially in 1st step, followed by non-chlorine bleaching)	1.0	15	1.5	30
4	Sulfite process, Cl_2	ND	ND	ND	ND
5	Kraft process, ClO_2	0.06	2	0.2	10
6	Sulfite process, either ClO_2 or totally chlorine-free (TCF)	ND	ND	ND	ND
7	Thermo-mechanical process, lignin-saving chemical treatment	ND	ND	ND	ND
8	Paper recycling with contaminated waste paper	ND	30**	ND	ND
9	Paper recycling with modern paper	ND	ND	ND	ND

* Raw effluent

** Wastewater from deinking system

Table II.7.5 PCDD/PCDF emission factors for source category 7a Pulp and Paper Products

7a	**Pulp and Paper Production**	**$EF_{Product}$ µg TEQ/t product**
	Classification	
1	Kraft process, Cl_2 , non-wood, PCP-contaminated fibers	30
2	Kraft process, Cl_2	10
3	Mixed technology (Cl_2 partially in 1st step, followed by non-chlorine bleaching)	3
4	Sulfite process, Cl_2	1
5	Kraft process, ClO_2	0.5
6	Sulfite process, either ClO_2 or totally chlorine-free (TCF)	0.1
7	Thermo-mechanical process, lignin-saving chemical treatment	1
8	Recycling paper from contaminated waste paper	10
9	Recycling paper from modern paper	3

Level of confidence

Emission factors for this source category are associated with a medium level of confidence for all classes, as they are based on a few reported data from a limited number of experiments with a limited geographical coverage, but not requiring expert judgment.

7b Chlorinated Inorganic Chemicals

For groups 7b through 7h, the following definitions of classes should be applied:

Guidance for classification of sources

Low-end technologies: No information available, or processes (reactions, purification steps and wastewater and waste treatment) are not controlled in respect to the formation of PCDD/PCDF or other unintentional POPs. Chemical feedstocks, air emissions, wastewater, residues and products are not monitored for PCDD/PCDF, other unintentional POPs or indicator substances.

Mid-range technologies: Processes (reactions and purifications steps including prevention by process- and production-integrated measures and wastewater and waste treatment) are controlled to some extent to limit releases. Parameters of these processes (*e.g*. feedstock; temperature; presence or use of chlorine in some form and, if, used, its concentration) are also controlled to reduce formation and release of unintentional POPs. Process inputs and emissions to air, wastewater, residues and products are monitored to some extent for PCDD/PCDF, other unintentional POPs or indicator substances.

High-end technologies: Processes (reactions and purifications steps including prevention by process- and production-integrated measures and wastewater and waste treatment) are optimized for low or no releases. Parameters of these processes (*e.g*. feedstock; temperature; presence or use of chlorine in some form and, if, used, its concentration) are optimized for minimum formation and release of unintentional POPs. Chemicals, products or by-products, emissions to air, wastewater and residues are monitored for PCDD/PCDF, other unintentional POPs or indicator substances. A refining step is used where appropriate to minimize unintentional POPs in the final chemical, product or by-product. Process residues should be handled in an environmentally sound manner, as described in the guidance on the BAT and BEP.

Elemental Chlorine (Cl_2)

Production of Cl_2 (CAS 7782-50-5) is the first step in producing chemicals and consumer goods that contain chlorine, as well as those for which some form of chlorine is used during their production. Global production of Cl_2 was estimated to be 81.2 million tons per year in 2012 (CMAI 2011a) and its uses, on a worldwide basis, are as follows (Beal and Linak 2011):

- Almost 35% is used in the EDC/VCM/PVC production chain – production of ethylene dichloride (EDC), which is used to make vinyl chloride (VCM) that is polymerized to produce polyvinyl chloride (PVC);
- 15% is used in the manufacture of isocyanates and propylene oxide, both of which are building blocks for polyurethane;
- 20% is used to produce other organic derivatives;
- 20% is used in the production of inorganic chemicals; and
- The remaining 10% is used in a variety of processes, such as water and wastewater treatment.

Uses of Cl_2 vary greatly by country and region. In the chlor-alkali process, Cl_2 and caustic soda [sodium hydroxide (NaOH)] are produced in a mass ratio of 1:1.1 by the electrolysis of brine (sodium chloride). Factors that can influence PCDD/PCDF formation and release in the chlor-alkali process include process design and direct contact of Cl_2 with reactive materials, such as graphite electrodes and certain seals, gaskets, lubricants, etc.

Electrodes made of graphite, a form of elemental carbon, which often included tar as binder pitch, were widely used until the 1970s when, in many countries, they were replaced by titanium electrodes. Due in part to their contribution to PCDD/PCDF formation and release, graphite electrodes are not considered Best Available Technique (BAT). Limited data show that far lower levels of PCDF may also be formed when titanium electrodes are used, perhaps through reactions of elemental chlorine with reactive gaskets and seals (USEPA 2004).

More detailed descriptions of the three main chlor-alkali processes are presented in the BAT&BEP Guidelines.

Emission Factors

Emission factors are derived for four classes of Cl_2 production via the chlor-alkali process: one class that uses graphite electrodes without regard for equipment and operational standards, and three classes that use titanium electrodes. Revised or newly added emission factors are highlighted in red.

Table II.7.6 PCDD/PCDF emission factors for source category 7b Elemental Chlorine Production

7a Elemental chlorine (Cl_2)	Emission Factors (µg TEQ/ECU*)				
Classification	**Air**	**Water**	**Land**	**Product**	**Residue**
1. Chlorine/chlor-alkali production using graphite electrodes	ND	ND	ND	ND	20,000 µg TEQ/t sludge 1,000 µg TEQ/ECU
2. Chlorine/chlor-alkali production using titanium electrodes					
2a Low-end technologies	**ND**	**17**	**ND**	**ND**	**27**
2b Mid-range technologies	**ND**	**1.7** **120 pg TEQ/L**	**ND**	**ND**	**1.7**
2c High-end technologies	**ND**	**0.002**	**ND**	**ND**	**0.3**

*Electrochemical unit (ECU) consists of 1 ton of chlorine and 1.1 tons of caustic soda (NaOH)

Level of Confidence

Emission factors in this section are associated with a low level of confidence for all classes since they are based on a low data range with limited geographical coverage.

7c Chlorinated Aliphatic Chemicals

Ethylene Dichloride (EDC), Vinyl Chloride Monomer (VCM) and Polyvinyl Chloride (PVC)

Approximately 35% of global production of elemental chlorine is consumed by the production of ethylene dichloride (EDC) (CAS 107-06-2), vinyl chloride monomer (VCM) (CAS 75-01-4) and polyvinyl chloride (PVC) (CAS 9002-86-2) (Beal and Linak 2011). EDC is used almost exclusively for producing VCM and VCM is used almost exclusively in the production of PVC resin (Nexant 2009). In 2009, worldwide production of PVC was estimated at 32.3 million tons per year (GBI 2011).

PVC is produced by two major pathways:

- The EDC/VCM/PVC production chain uses ethylene derived from petroleum or natural gas as its primary feedstock and accounts for about two-thirds of global PVC production; and
- The acetylene/VCM/PVC production chain which uses acetylene derived from coal as the primary feedstock and accounts for the remaining one-third of global PVC production (CMAI 2011b).

The EDC/VCM/PVC production chain consists of five major processes:

1. EDC production

   a. Direct chlorination of ethylene using elemental chlorine in the presence of an iron catalyst; and/or

   b. Oxychlorination of ethylene using hydrogen chloride (HCl) and air or oxygen in the presence of a copper catalyst;

2. Purification of EDC;
3. VCM production via thermal cracking of EDC, which also produces HCl that may be recycled into the oxychlorination process;
4. Purification of VCM; and
5. PVC production via polymerization of VCM.

Oxychlorination of ethylene to produce EDC has been described as the most favorable process step in the chemical industry for the formation of PCDD/PCDF (UNEP 2005). However, PCDD/PCDF are also known to occur in other processes in the EDC/VCM/PVC production chain (Weiss and Kandle 2006).

Within the EDC/VCM/PVC chain, most EDC production is a balanced mix of direct chlorination and oxychlorination, although some sites are direct chlorination only, or oversized for oxychlorination. Most EDC production is integrated with VCM production on the same site. However, some facilities produce only EDC and ship it elsewhere, and, perhaps more commonly, VCM production facilities ship their VCM elsewhere for polymerization into PVC. PCDD/PCDF can be released to one or more vectors from the production of EDC, VCM, and PVC, as detailed in Annex 48.

The acetylene/VCM/PVC production chain entails the following major processes:

1. VCM production via the reaction of acetylene with HCl in the presence of a mercuric chloride catalyst;
2. Purification of VCM; and
3. Polymerization of VCM to form PVC.

The acetylene/VCM/PVC production chain is largely used in China, where it accounts for 81% of total PVC production capacity (CMAI 2011b). Little information is available on PCDD/PCDF releases from this production chain other than limited data on releases from acetylene production (Lee *et al*. 2009, Jin *et al*. 2009) and in wastewater treatment sludge (USEPA 2000). More detailed descriptions of EDC, VCM and PVC production processes are given in Annex 48 and in the BAT&BEP Guidance.

Emission Factors

Emission factors for production of EDC, VCM and PVC are presented in Tables II.7.7-II.7.10, according to four types of facilities – EDC/VCM/PVC facilities, EDC/VCM facilities, EDC-only facilities and PVC-only facilities. Revised or newly added emission factors are highlighted in red.

The derivation of emission factors presented in Tables II.7.7-II7.10 is explained in Annex 48. As parties and facilities evaluate their operations they should note that any facility may have a mixture of classes of operation. Generally, analytical data should be required to support a claim of class 3.

For on-site hazardous waste incinerators and boilers used to generate heat and power, relevant information should be gathered and included in Source Group 1 – Waste Incineration and Source Group 3 – Power Generation and Heating, respectively.

Table II.7.7 PCDD/PCDF emission factors (EF_{Air}) for source category 7c EDC/VCM/PVC Production: Releases to Air from Vent or Liquid/Vent Combustors or Thermal Oxidizers and Halogen Acid Furnaces

7c EDC, VCM and PVC Production	EDC, EDC/VCM and EDC/VCM/PVC Vent and Liquid-Vent Combustors or Thermal Oxidizers		PVC-Only[11] Vent Combustors or Thermal Oxidizers		Halogen Acid Furnaces
		Flue Gas Conc.		Flue Gas Conc.	Flue Gas Conc.
Classification	**µg TEQ/t VCM**	**ng TEQ/ Nm^3**	**µg TEQ/t PVC**	**ng TEQ/ Nm^3**	**ng TEQ/ Nm^3**
1. Low-end technologies	5	5	1	1	0.5
2. Mid-range technologies	0.5	0.5	0.1	0.1	0.06
3. High-end technologies	0.05	0.1	0.02	0.02	0.02

Table II.7.8 PCDD/PCDF emission factors (EF_{Water}) for source category 7c EDC/VCM/PVC Production: Releases to Water via Wastewater Effluent

7c EDC, VCM, and PVC Production	EDC, EDC/VCM and EDC/VCM/PVC production from sites with oxychlorination reactors[A]		Suspension, Dispersion or Emulsion PVC-only	
		Concentration		Concentration
Classification	**µg TEQ/t EDC**	**ng TEQ/L effluent**	**µg TEQ/t PVC**	**ng TEQ/L effluent**
1. Low-end technologies	25	5	0.03	0.01
2. Mid-range technologies	2.5	0.5	0.003	0.001
3. High-end technologies	0.5	0.1	0.0003	0.0001

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

Table II.7.9 PCDD/PCDF emission factors ($EF_{Residue}$) for source category 7c EDC/VCM/PVC Production: Releases to Residues

7c EDC, VCM and PVC Production	EDC, EDC/VCM, and EDC/VCM/PVC Facilities µg TEQ/t EDC from sites with oxychlorination reactors[A]		PVC-only µg TEQ/t PVC
	Waste Water Treatment Solids	Spent Catalyst	Waste Water Treatment Solids

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[11] As used here, the term "PVC-only" refers to facilities that polymerize VCM received from other sources.

Classification	Fixed-bed[B]	Fluidized-bed[C]	Fixed-bed[B]	
1. Low-end technologies	**0.75**	**4**	**8**	**0.095**
2. Mid-range technologies	**0.2**	**2**	**0.85**	**0.06**
3a. High-end technologies (if solids are incinerated)	**NA**			
3b. High-end technologies (if solids are not incinerated)	**0.095**	**0.4**	**0.02**	**0.005**

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

[B] Solids derived from an EDC facility utilizing a fixed-bed oxychlorination catalyst

[C] Solids derived from an EDC facility utilizing a fluidized-bed oxychlorination catalyst

Table II.7.10 PCDD/PCDF emission factors ($EF_{Product}$) for source category 7c EDC/VCM/PVC Production: Releases to Products

7c EDC, VCM and PVC Production	µg TEQ/t EDC, VCM or PVC sold			
	EDC		VCM	PVC
Classification	**Produced by oxychlorination or mixed direct chlorination and oxychlorination**	**Produced by Direct chlorination only**		
1. Low-end technologies	**2**	**ND**	**NA**	**ND**
2. Mid-range technologies	**0.2**	**ND**	**NA**	**ND**
3. High-end technologies	**0.006**	**ND**	**NA**	**NA**

Level of confidence

Emission factors in this source category are associated with a low level of confidence for all classes, as emission factors are based on a low data range derived from a limited geographical coverage.

7d Chlorinated Aromatic Chemicals

Chlorobenzenes

Chlorobenzenes are produced commercially by reacting Cl_2 with liquid benzene in the presence of a catalyst such as ferric chloride ($FeCl_3$). The predominant products of this reaction are chlorobenzene, HCl, 1,2-dichlorobenzene (o-dichlorobenzene) (CAS 95-50-1) and 1,4-dichlorobenzene (p-dichlorobenzene) (CAS 106-46-7). As this direct chlorination process is continued, 1,2,4-trichlorobenzene (CAS 120-82-1), other tri-, tetra-, and pentachlorobenzenes, and, finally, hexachlorobenzene are formed. Total global production of chlorobenzenes in 2003 is estimated at 640,000 tons (China Chemical Reporter 2004).

For 1,4-dichlorobenzene, the largest use may be in the production of poly(*p*-phenylene) sulfide, a thermoplastic polymer in wide use because of its resistance to chemical and thermal attack. It is also used as an insecticide to control moths, moulds, mildew, and as a disinfectant and odor control agent in waste containers and restrooms (Rossberg *et al.* 2006).

Emission Factors

A default emission factor is shown in Table II.7.11 for 1,4-Dichlorobenzene, and further details on its derivation are presented in Annex 48.

Table II.7.11 PCDD/PCDF emission factors for source category 7d Chlorobenzene Production

7d	**Chlorobenzene Production**	**Emission Factors (µg TEQ/t product)**				
	Classification	**Air**	**Water**	**Land**	**Product**	**Residue**
1	1,4-Dichlorobenzene (1,4-DCB, *p*-dichlorobenzene or *p*-DCB)	ND	ND	NA	39	ND

Level of confidence

The emission factor is associated with a medium level of confidence, as it is based on a low data range; it is not based on expert judgment, but derived from a limited geographical coverage.

Polychlorinated Biphenyls (PCBs)

The total global production of PCBs is estimated at 1.3 to 2 million tons (Breivik *et al.* 2002, Fiedler 2001). PCBs have been used for a wide range of closed applications (transformers, capacitors) and open applications (sealants, caulking, carbonless paper, plasticizers in paints and cements, casting agents, flame retardant in fabric and heat stabilizing additives for PVC electrical insulation, adhesives, railway sleepers) (Erickson and Kaley 2011). Although PCB production ceased in the 1980s, much PCB-containing equipment remains in use, materials containing PCBs are being used, and PCB wastes are still awaiting disposal.

PCDD/PCDF in commercial PCBs consist mainly of PCDF in the µg/kg to mg/kg range, along with low PCDD concentrations (Takasuga *et al.* 2005, Huang *et al.* 2011, Johnson *et al.* 2008, Wakimoto *et al.* 1988). The global production of 1.3 to 2 million tons PCBs contained approximately 10,400 to 16,000 kg WHO-TEQ mainly from dioxin-like PCBs (Weber *et al.* 2008). PCDD/PCDF concentrations in used PCBs are largely unknown. Limited data are available on PCDF levels in used PCBs, indicating that, for transformers, the levels might be similar as those found in used PCBs (Huang *et al.* 2011, Masuda *et al.* 1986). As shown in Table II.10.1, the dioxin-like TEQ contribution from PCDF in technical PCBs is normally below 10%. When commercial PCBs are subjected to elevated temperatures, PCDD/PCDF concentrations increase as documented for heat exchange fluids in the Yusho incident, where PCDF TEQ levels had considerably increased, reaching similar TEQ levels as for dl-PCB (Masuda *et al.* 1986). PCDF formation by thermal treatment of PCB can result in a TEQ increase of the PCB mixture of up to 50 fold (Weber 2007). Sites where PCBs are used or PCB-containing equipment is stored, dismantled or disposed of can generate local contamination and potential hotspots (see Source Group 10).

The first step in estimating the stock and releases of PCDD/PCDF associated with the use and storage of PCB-containing equipment is to compile a national inventory of the equipment and possibly other PCB legacies. Based on the PCB inventory, total TEQ in this stock can be calculated according to Table II.10.2. The inventory data can be used in combination with PCB leakage rates to estimate the quantity of PCDD/PCDF and dioxin-like PCBs released annually from the inventoried PCB equipment. The PCB leakage rates depend on a number of factors including the age of the equipment, conditions of exploitation and storage, climatic conditions etc. The precise impact of most of these factors is not well studied. For a preliminary assessment of PCB releases into the environment, emission factors given in the EMEP/EEA Atmospheric Emission Inventory Guidebook (2009) can be used (Table II.10.1).

Local circumstances will determine whether the leaked PCBs and PCDD/PCDF are released to air, water or land or sent to disposal.

Pentachlorophenol (PCP) and Sodium Pentachlorophenate (PCP-Na)

PCP or "penta" (CAS 87-86-5) and PCP-Na (CAS 131-52-2) are used as pesticides and as preservatives for *e.g*. wood (indoor and outdoor), leather, textiles (including cotton or wool) and for killing snails in areas where schistosomiasis is epidemic (Zheng *et al.* 2008, 2011). PCP is also used to produce PCP-Na and pentachlorophenol laurate (PCPL), which is used on textiles and other fabrics (van der Zande 2010).

While there are no recent data on global production, PCP production is estimated at 7,257 tons/year in the U.S. (van der Zande 2010). In 2010, Mexico produced approximately 7,000 tons/year, approximately 80% of which were exported (B. Cardenas, personal communication, 26 November 2012). In China, PCP production was of 10,000 tons/year in 1997 (Ge *et al.* 2007). PCP is produced by several methods, including the following:

1. Reaction of Cl_2 with liquid phenol, chlorophenol or a polychlorophenol at 30-40°C to produce 2,4,6-trichlorophenol, which is then converted to PCP by further chlorination at progressively higher temperatures in the presence of catalysts (aluminum, antimony, their chlorides, and others) (Borysiewicz 2008);

2. Alkaline hydrolysis of hexachlorobenzene (HCB) in methanol and dihydric alcohols, in water and mixtures of different solvents in an autoclave at 130 - 170°C (Borysiewicz 2008); and

3. Thermolysis of hexachlorocyclohexane (HCH), including a chlorination step and hydrolysis (Wu 1999).

PCP-Na was produced until 1984 using the alkaline hydrolysis of hexachlorobenzene. Now, however, it is produced by dissolving PCP flakes in sodium hydroxide solution (Borysiewicz 2008). It has been suggested that post-production processing of PCP flakes from the latter process accounted for more extensive exposure to PCP and its contaminants than did production (Ruder 2011).

PCDD/PCDF are by-products in all of these manufacturing methods (Borysiewicz 2008). In addition, the method based on alkaline hydrolysis of HCB can result in the presence of HCB in the resulting PCP. Commercial PCP may contain up to 0.1% of PCDD/PCDF, which are released to the air from PCP-treated products, released to water when PCP-treated textiles and other products are washed, and concentrated in the sludge of wastewater facilities that treat the washwater. PCP-derived PCDD/PCDF are released to air and land from in-service wood products, such as utility poles and railroad ties (Borysiewicz 2008), when sewage sludge is land applied, and when PCP-treated products are burned.

PCDD/PCDF may also be brought into a country through the import of PCP as well as PCP-treated products such as wood and wood products, furniture, textiles, and leather. Tracing these flows can be very difficult. The impact on emission factors of burning PCP-contaminated wood can be seen in source category 3d - Household Heating and Cooking with Biomass. PCP-treated materials also contribute to higher releases from open burning processes as can be seen in source category 6b - Waste Burning and Accidental Fires.

Emission Factors

Emission factors for PCP and PCP-Na are presented in Table II.7.14. Revised or newly added emission factors are highlighted in red. For the use of PCP for agricultural or related purposes, releases to land of PCDD/PCDF can be estimated by using the $EF_{Product}$ as EF_{Land}.

Table II.7.14 PCDD/PCDF Emission Factors for source category 7d PCP and PCP-Na Production

7d	PCP and PCP-Na Production	Emission Factors (µg TEQ/t product)				
Classification		**Air**	**Water**	**Land**	**Product**	**Residue**
1	Pentachlorophenol (PCP)	ND	ND	ND	**634,000**	ND
2	Pentachlorophenol, sodium salt (PCP-Na)	ND	ND	ND	**12,500**	ND

Level of Confidence

Emission factors in this source category are associated with a medium level of confidence, as they are based on a low data range and are derived from a limited geographical coverage.

2,4,5-Trichlorophenoxyacetic Acid (2,4,5-T) and 2,4,6-Trichlorophenol

2,4,5-T (CAS 93-76-5), an herbicide used primarily as a defoliant, is the most important derivative of 2,4,5-trichlorophenol (CAS 95-95-4). Today, there are only a few production sites of trichlorophenol. While 2,4,5-T is widely perceived as being contaminated with only 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), substantial concentrations of other PCDD/PCDF congeners have been identified (Pignatello and Huang 1993).

Hotspots in soil that may exist at former 2,4,5-T production, storage and handling sites should be addressed in Source Group 10 – Contaminated Sites and Hotspots.

Emission Factors

Due to lack of data, emission factors have been derived only for releases in products, as shown in Table II.7.15. For the use of 2,4,5-T for agricultural or related purposes, releases to land of PCDD/PCDF can be estimated by using the $EF_{Product}$ as EF_{Land}.

Table II.7.15 PCDD/PCDF Emission Factors for source category 7d 2,4,5-T and 2,4,6-Trichlorophenol Production

7d	2,4,5-T and 2,4,6-Trichlorophenol Production	Emission Factors (µg TEQ/t product)				
Classification		**Air**	**Water**	**Land**	**Product**	**Residue**
1	2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	ND	ND	ND	7,000	ND
2	2,4,6-Trichlorophenol	ND	ND	ND	700	ND

Level of confidence

Emission factors are associated with a medium level of confidence, as they are based on a low data range; they are not based on expert judgment, but are derived from a limited geographical coverage.

Chloronitrofen, Chlornitrofen, or 2,4,6-Trichlorophenyl-4-nitrophenylether (CNP)

CNP (CAS 1836-77-7) has been used as an alternative for pentachlorophenol and applied extensively in rice paddies in Japan. Production of CNP begins with the production of 2,4,6-trichlorophenol (CAS 88-06-2). 2,4,6-trichlorophenol is reacted with potassium hydroxide to form potassium 2,4,6-trichlorophenolate. The latter chemical is reacted with 4-fluoronitrobenzene in the presence of a copper catalyst to form 2,4,6-trichlorophenyl *p*-nitrophenyl ether (Suzuki and Nagao 2005).

Emission Factors

Due to insufficient information, only emission factors for releases in product were derived, as shown in Table II.7.16. Revised or newly added emission factors are highlighted in red. For the use of CNP for agricultural or related purposes, releases to land of PCDD/PCDF can be estimated by using the $EF_{Product}$ as EF_{Land}.

Table II.7.16 PCDD/PCDF Emission Factors for source category 7d CNP Production

7d	**CNP Production**	**Emission Factors (µg TEQ/t product)**				
	Classification	**Air**	**Water**	**Land**	**Product**	**Residue**
1	Low-end technologies	ND	ND	ND	**9,200,000**	ND
2	Mid-range technologies	ND	ND	ND	**4,500**	ND

Level of confidence

Emission factors are associated with a medium level of confidence, as they are based on a low data range; they are not based on expert judgment, but are derived from a limited geographical coverage.

Pentachloronitrobenzene (PCNB) (Quintozene)

PCNB (CAS 82-68-8), also known by other names including quintozene and terrachlor, is a broad-spectrum, contact fungicide used on a wide range of crops, such as turf, peanuts, cole crops (*e.g.*, cabbage), rice, potatoes and cotton. It is used to treat both soil and seeds as well as for foliar application. However, due in part to PCDD/PCDF contamination, PCNB has been banned for a variety of uses in several countries, including the U.S., Canada, Japan and Germany.

PCNB is produced by the reaction in chlorosulfuric acid of nitrobenzene and Cl_2 with iodine as a catalyst. PCNB can also be produced by the nitration of pentachlorobenzene.

High concentrations of PCDD/PCDF have been detected in studies conducted in Australia (Holt *et al*. 2010), China (Huang *et al*. 2012), and Japan (MAFF 2002). The latter two studies also found high concentrations of dioxin-like PCBs. In addition, a study of PCNB exposure to sunlight found that PCDD/PCDF TEQ increased by more than 800% (Holt *et al*. 2011).

Emission Factors

For the production of PCNB, PCDD/PCDF emission factors are shown in Table II.7.17 and PCB emission factors are shown in Annex 48. Revised or newly added emission factors are highlighted in red.

For the use of PCNB is for agricultural or related purposes, release to land of both PCDD/PCDF and PCBs can be estimated by using the $EF_{Product}$ as EF_{Land}. Similarly, for aquacultural or related purposes, release to water can be estimated by using the $EF_{Product}$ as EF_{Water}.

Table II.7.17 PCDD/PCDF Emission Factors for source category 7d Pentachloronitrobenzene Production

7d	**Pentachloronitrobenzene Production**	**Emission Factors (µg TEQ/t product)**				
Classification		**Air**	**Water**	**Land**	**Product**	**Residue**

1	Low-end production technologies	ND	ND	ND	**5,600**	ND
2	Mid-range production technologies	ND	ND	ND	**2,600**	ND
3	High-end production technologies	ND	ND	ND	**260**	ND

Level of confidence

Emission factors in this section are associated with a medium level of confidence, as emission factors are based on a moderate data range with a broad geographical distribution.

2,4-Dichlorophenoxyacetic Acid (2,4-D) and Derivatives

2,4-Dichlorophenoxyacetic acid (2,4-D, CAS 94-75-7) and its derivatives are systemic herbicides used to control broadleaf weeds. 2,4-D is one of the world's most widely used pesticides (Industry Task Force 2012).

2,4-D is commonly prepared by the condensation of 2,4-dichlorophenol with monochloroacetic acid in a strongly alkaline medium at moderate temperatures. It is also produced by the chlorination of phenoxyacetic acid, but this method leads to a product with a high content of 2,4-dichlorophenol and other impurities. Higher reaction temperatures and alkaline conditions during the manufacture of 2,4-D increase the formation of PCDD/F. The alkali metal salts of 2,4-D are produced by the reaction of 2,4-D with the appropriate metal base. Amine salts are obtained by reacting amine and 2,4-D in a compatible solvent. Esters are formed by acid-catalysed esterification with azeotropic distillation of water or by direct synthesis in which the appropriate ester of monochloroacetic acid is reacted with dichlorophenol to form the 2,4-D ester (IPCS 1989). The following include some of the more commonly used derivatives of 2,4-D: 2,4-D sodium salt (CAS 2702-72-9); 2,4-D diethyl amine (CAS 2008-39-1); 2,4-D dimethylamine salt (CAS 2008-39-1); 2,4-D isopropyl ester (CAS 94-11-1); 2,4-D triisopropyl acid; 2,4-D butoxyethyl ester (CAS 1929-73-3); 2,4-D isooctyl ester (CAS 25168-26-7); and 2,4-D ethylhexyl ester (CAS 1928-43-4). 2,4-D was first marketed in 1944. Off-patent for many years, 2,4-D and its derivatives are manufactured by many different companies around the world.

Emission Factors

For the production of 2,4-D and its derivatives, PCDD/PCDF emission factors are presented in Table II.7.18. Revised or newly added emission factors are highlighted in red.

For uses of 2,4-D and its derivatives for agricultural or related purposes, release to land can be estimated by using the $EF_{Product}$ as EF_{Land}. Similarly, for aquacultural uses, release to water can be estimated by using the $EF_{Product}$ as EF_{Water}.

Table II.7.18 PCDD/PCDF Emission Factors for source category 7d 2,4-D and Derivatives

7d	2,4-D and Derivatives	Emission Factors (µg TEQ/t product)				
Classification		Air	Water	Land	Product	Residue
1	Low-end production technologies	ND	ND	ND	**5,688**	ND
2	Mid-range production technologies	ND	ND	ND	**170**	ND
3	High-end production technologies	ND	ND	ND	**0.1**	ND

Level of confidence

Emission factors in this section are associated with a medium level of confidence, as emission factors are based on a moderate data range with a broad geographical distribution.

More detailed information on PCDD/PCDF contamination of other organochlorine pesticides can be found in Annex 2.

Chlorinated Paraffins (CPs)

CPs are straight-chain hydrocarbons that have been chlorinated. Chlorinated paraffins are classified according to their carbon-chain length and percentage of chlorination, with carbon-chain lengths generally ranging from C_{10} to C_{30} and chlorination from approximately 35% to greater than 70% by weight. Around 40 CAS numbers have been used to describe the whole chlorinated paraffin family, *e.g*., CPs of unspecified length are CAS 63449-39-8.

CPs are made by reacting Cl_2 with paraffin fractions obtained from petroleum distillation. The three most common commercial feedstocks used are short-chain (C_{10-13}), medium-chain (C_{14-17}) and long-chain (C_{18-30}) paraffins. Global production of CPs is estimated at 1 million tons/yr, some 70% of which is produced in China (Takasuga *et al*. 2012). The largest use of CPs is in industrial cutting fluids, particularly in the manufacture of automobiles and automobile parts. In addition, they are used in commercial paints, adhesives, sealant and caulks as well as plasticizers in PVC and flame retardants in other plastics and rubber. Relatively high concentrations of PCDD/PCDF, total PCBs and HCB have been reported in samples of technical long-chain CPs (Takasuga *et al*. 2012).

Emission Factors

For the production of CPs, PCDD/PCDF emission factors are shown in Table II.7.19. Revised or newly added emission factors are highlighted in red. Emission factors for other unintentional POPs releases are presented in Annex 48.

Table II.7.19 PCDD/PCDF Emission Factors for source category 7d Chlorinated Paraffins Production

7d	Chlorinated Paraffins Production	Emission Factors (µg TEQ/t product)				
Classification		Air	Water	Land	Product	Residue
1	Low-end production technologies	ND	ND	ND	ND	ND
2	Mid-range production technologies	ND	ND	ND	**500**	ND
3	High-end production technologies	ND	ND	ND	**140**	ND

Level of confidence

Emission factors in this section are associated with a low level of confidence, as emission factors are based on a small data range with a limited geographical distribution.

p-Chloranil (2,3,5,6-tetrachloro-2,5-cyclohexadiene-1,2-dione)

p-Chloranil (CAS 118-75-2) is used as an intermediate in the production of medicines, pesticides, and dioxazine dyes. It is also used as a fungicide and for seed treatment, although such uses are prohibited in some countries. In China, about 2,000 tons of chloranil are produced and used as a fungicide, as an intermediate in the synthesis of medicines and pesticides, and as an oxidizing agent used in organic synthesis, particularly for dye intermediates (Liu *et al.* 2012). Two methods for producing *p*-chloranil are as follows:

1. The process of direct chlorination of phenol using Cl_2, which produces both *o*- and *p*-chloranil was developed and used in Germany until 1990. This may still be used by producers in other countries.

2. The more widely used process begins with the conversion of phenol to hydroquinone, followed by the reaction of hydroquinone with Cl_2 or hydrogen peroxide and hydrochloric acid to form *p*-chloranil.

PCDD/PCDF contamination in chloranil is transferred to dyestuffs, pigments, inks, etc. and other products made from chloranil (see chloranil-derived pigments and dyes below). PCDD/PCDF in chloranil-derived materials are further transferred into the production processes of textiles, polymers/plastics, and packaging materials (paper, tin cans, etc.) and released in process outputs (see, for example, Source Category 7g – Textile Production). When textiles, clothing and other consumer goods treated with chloranil-based pigments and dyes are washed, some portion of the PCDD/PCDF is carried into domestic and municipal wastewater, where it contributes to PCDD/PCDF in wastewater treatment effluents and sludge. When the consumer goods are discarded or recycled, the PCDD/PCDF that originated during chloranil production adds to PCDD/PCDF contamination in disposal and recycling processes. In paper recycling and textile production and dyeing, PCDD/PCDF will be released into water and/or concentrated in the residue (sludge).

Emission Factors

Due to lack of data, emission factors for *p*-chloranil are derived only for releases to product. Revised or newly added emission factors are highlighted in red.

Table II.7.20 PCDD/PCDF Emission Factors for source category 7d *p*-Chloranil Production

7d	***p*-Chloranil Production**	**Emission Factors (µg TEQ/t product)**				
Classification		**Air**	**Water**	**Land**	**Product**	**Residue**
1	Direct chlorination of phenol	ND	ND	ND	400,000	ND
2	Chlorination of hydroquinone with minimal purification	ND	ND	ND	**1,500,000**	ND
3	Chlorination of hydroquinone with moderate purification	ND	ND	ND	**26,000**	ND
4	Chlorination of hydroquinone with advanced purification	ND	ND	ND	**150**	ND

Level of confidence

Emission factors are associated with a medium level of confidence, as they are based on a low data range; they are not based on expert judgment, but are derived from a limited geographical coverage.

Phthalocyanine dyes and pigments

Phthalocyanine dyes and pigments had a global production rate of about 420,000 tons in 2011 (Linak *et al.* 2011, The Freedonia Group 2009). They are prepared by variations of the following methods:

- Reaction of phthalonitrile with metal or metal salts;
- Reaction of phthalic anhydride, phthalic acid or phthalimide, tetrachlorophthalic anhydride with *e.g*. specific organics, urea, metal salt and catalyst;
- Reaction of metal-free phthalocyanine or replaceable metal phthalocyanine with another metal.

Copper phthalocyanine, a blue pigment, is generally produced using the second method. The phthalic anhydride/imide, a metal salt, urea and a catalyst are heated at 170-200^{0}C for about four hours in a solvent such as trichlorobenzene, nitrobenzene or chloronaphthalene. The blue of copper phthalocyanine is shifted towards green by replacing hydrogen atoms on the aromatic rings with chlorine (*e.g*. pigment green 7) or chlorine and bromine (*e.g*. pigment green 36). This is accomplished through direct chlorination of copper phthalocyanine by passing Cl_2 into an $AlCl_{3/}NaCl$ mixture at 180-200^{0}C (Jain 2011). PCDD/PCDF have been detected in samples of copper phthalocyanine and phthalocyanine green (Ni *et al.* 2005), as well as nickel phthalocyanine (Hutzinger and Fiedler 1991).

Emission Factors

Due to lack of data, PCDD/PCDF emission factors for phthalocyanine-derived dyes and pigments are presented only for releases in products. Revised or newly added emission factors are highlighted in red. Emission factors for other unintentional POPs are included in Annex 48.

Table II.7.21 PCDD/PCDF Emission Factors for source category 7d Phthalocyanine Dyes and Pigments Production

7d	Phthalocyanine Dyes and Pigments Production	Emission Factors (µg TEQ/t product)				
	Classification	**Air**	**Water**	**Land**	**Product**	**Residue**
1	Phthalocyanine copper (CAS 147-14-8)	ND	ND	ND	**70**	ND
2	Phthalocyanine green (CAS 1328-45-6)	ND	ND	ND	**1,400**	ND

Tetrachlorophthalic acid (TCPA) and related pigments

TCPA is the primary feedstock for the production of a range of pigments. While no PCDD/PCDF data are available for TCPA, unintentional HCB concentrations as high as 3,000,000 µg/kg have been detected (Government of Japan 2006, 2007). Additional information on HCB concentrations in TCPA and corresponding emission factors are included in Annex 48.

Dioxazine dyes and pigments

Dioxazine dyes and pigments are produced through the reaction of *p*-chloranil with aromatic amines in the presence of a base. Tests on some of these dyes and pigments in the early 1990s showed PCDD/PCDF concentrations in the range 1 to 60 µg TEQ/kg, attributed to the use of PCDD/PCDF-contaminated *p*-chloranil produced by the chlorination of phenol (US EPA 2006a, Krizanec and Le Marechal 2006). Subsequently, an alternate process was developed for producing chloranil with lower PCDD/PCDF content through the reaction of hydroquinone with HCl. Dioxazine pigments and dyes made using the more contaminated chloranil are listed in Table II.7.22, along with their PCDD/PCDF content. Revised or newly added emission factors are highlighted in red.

Table II.7.22 PCDD/PCDF Emission Factors for source category 7d Dioxazine-Based Pigments Production

7d	Dioxazine-Based Pigments Production	Emission Factors (µg TEQ/t product)				
Classification		**Air**	**Water**	**Land**	**Product**	**Residue**
1	Blue 106 (CAS 6527-70-4)	ND	ND	ND	**35,000**	ND
2	Blue 108 (CAS 1324-58-9)	ND	ND	ND	**100**	ND
3	Violet 23 (Carbazole violet) (CAS 6358-30-1)	ND	ND	ND	**12,000**	ND

Level of confidence

Emission factors are associated with a medium level of confidence, as they are based on a low data range; they are not based on expert judgment, but are derived from a limited geographical coverage.

Triclosan [5-chloro-2-(2,4-dichlorophenoxy)phenol]

Triclosan (CAS 3380-34-5), a chlorophenoxy derivative, is produced by the reaction of 2,4,4'-trichloro-2'-methoxydiphenyl ether with aluminum chloride in benzene. Triclosan is used globally as an antibacterial and antifungal agent in consumer products, including soaps, deodorants, toothpastes, shaving creams, mouth washes, and cleaning supplies. It is also infused in an increasing number of consumer products, such as kitchen utensils, toys, bedding, socks, and trash bags.

Emission Factors

Emission factors are derived for three classes of production of triclosan. Revised or newly added emission factors are highlighted in red.

Table II.7.23 PCDD/PCDF Emission Factors for source category 7d Triclosan Production

7d	**Triclosan Production**	**Emission Factors (µg TEQ/t product)**				
	Classification	**Air**	**Water**	**Land**	**Product**	**Residue**
1	Low-end technologies	ND	ND	ND	**1,700**	**82,000**
2	Mid-range technologies	ND	ND	ND	**60**	ND
3	High-end technologies	ND	ND	ND	**3**	ND

Level of confidence

Emission factors are associated with a medium level of confidence, as they are based on a low data range; they are not based on expert judgment, but are derived from a limited geographical coverage.

7e Other Chlorinated and Non-Chlorinated Chemicals

Titanium Tetrachloride ($TiCl_4$) and Titanium Dioxide (TiO_2)

TiO_2 (CAS 13463-67-7) is the world's most widely used white pigment, with global production estimated to be 5 million tons in 2007 (USGS 2008). About 50% of TiO_2 is used in paints, varnishes and lacquer; 25% in paper and paperboard; and 20% in plastics (USEPA 2001).

TiO_2 is produced from TiO_2-rich ores, such as rutile or ilmenite, by either of two processes:

- The sulfate process entails digesting ilmenite ore or TiO_2-rich slag with sulfuric acid to produce a cake, which is purified and calcined to produce TiO_2 pigment. This process is less commonly used because it generates sulfuric acid wastes in as much as two times the product weight, resulting in the need for expensive treatment by neutralization before disposal of the wastes (UNEP 2007, USEPA 1995).
- The chloride process entails reacting elemental chlorine with rutile or high-grade ilmenite at 850°C to 950°C, using petroleum coke as a reductant. This produces $TiCl_4$ (CAS 7550-45-0) gas, which is then oxidized to form purified TiO_2. The chloride process is most commonly used due to its relative compactness, recycling of process materials, better product properties, and considerably lower generation of waste (UNEP 2007, USEPA 1995).

PCDD/PCDF formation is known to occur in the chloride process (Lakshmanan *et al.* 2004), and PCDD/PCDF have been detected in treated wastewater, wastewater treatment sludge, and filter press solids (USEPA 2001).

Emission Factors

Emission factors are derived for TiO_2 production via the chloride process and presented in Table II.7.24. Revised or newly added emission factors are highlighted in red.

Table II.7.24 PCDD/PCDF Emission Factors for source category 7e $TiCl_4$ and TiO_2 Production via the Chloride Process

7e	**$TiCl_4$ and TiO_2 Production**	**Emission Factors (µg TEQ/t product)**				
	Classification	**Air**	**Water**	**Land**	**Product**	**Residue**
1	Low-end technology	ND	**0.2**	ND	**0.0**	**42**
2	High-end technology	ND	**0.001**	ND	**0.0**	**8**

Level of confidence

Emission factors are associated with a medium level of confidence, as they are based on a low data range; they are not based on expert judgment, but are derived from a limited geographical coverage.

Caprolactam (2-Azacycloheptanone)

Caprolactam (CAS 105-60-2) is produced commercially by two methods. Only one entails the use of chlorine in some form: the reaction of HCl with nitrosylsulfuric acid to produce nitrosyl chloride which is then reacted with cyclohexane and HCl to produce cyclohexanone which undergoes further reactions to produce caprolactam. In 2010, global production of caprolactam was 3.8 million metric tons (SRI Consulting 2011). Virtually all caprolactam is used to produce Nylon 6. PCDD/PCDF have been detected in air emissions, process wastewater and in treated wastewater from caprolactam production facilities in two countries (Lee *et al.* 2009, Kawamoto 2002, Hong and Xu 2012). These findings suggest that PCDD/PCDF are likely also to occur in residues, including those from wastewater treatment.

Emission Factors

Table II.7.25 PCDD/PCDF Emission Factors for source category 7e Caprolactam Production

7e	**Caprolactam Production**	**Emission Factors (µg TEQ/t product)**				
	Classification	**Air**	**Water**	**Land**	**Product**	**Residue**
1	Caprolactam	**0.00035**	**0.50 pg TEQ/L**	ND	ND	ND

Level of confidence

Emission factors are associated with a medium level of confidence, as they are based on a low data range; they are not based on expert judgment, but are derived from a limited geographical coverage.

7f Petroleum Refining

The petroleum refining industry converts crude oil into refined products, including liquefied petroleum gas, gasoline, kerosene, aviation fuel, diesel fuel, fuel oils, lubricating oils, bitumen and feedstock for the petrochemical industry. The composition of petroleum (crude oil) can vary significantly depending on its source.

Petroleum refining processes that have been identified as PCDD/PCDF sources include the following (RTI International 2011, Jacobs Consultancy 2002):

- Stationary combustion sources, such as boilers and process heaters, generate heat and power by burning fuels derived from refinery processes; these sources are addressed in Source Group 3 Power Generation and Heating. Particular attention is needed in the development of the PCDD/PCDF inventory for this source category to avoid double counting of releases from power boilers.
- Coking units use heat to thermally crack heavy hydrocarbon streams to form lighter, more useful distillates such as heating oils or gasoline. Traditional fluid coking units are one of the largest vent emissions sources at a refinery, being comparable to emissions from the CCU regenerator.
- Catalytic reforming units are a series of catalytic reactors that turn naphtha into high-octane gasoline. The catalyst accumulates carbon (coke) so that it must be regenerated. In the continuous process, aged catalyst is continuously moved from the reactor to the regenerator where the carbon is burned from the catalyst with hot air/steam. Chlorine or organochlorines , such as tri- or perchloroethylene, are added to retain catalytic activity. While the catalytic reactors have no direct process vents, the catalyst regenerators do have such vents.
- Flares are compulsory safety equipment used both for safety reasons during upsets, start-up, shut down, and system blow-down and for managing the disposal of waste gases from routine operations.

PCDD/PCDF may be released to air from vent stacks and flares, captured in scrubbing systems and released to water in treated effluents, and released in residues such as exhausted catalysts and wastewater treatment sludge.

Emission Factors

Emission factors for calculating releases of PCDD and PCDF from petroleum refineries are presented below for the following processes:

- Flaring of gases released from the petroleum industry
- Catalytic reforming unit (including catalyst regenerator)
- Coking unit
- Refinery-wide wastewater treatment

PCDD/PCDF emission factors are listed in Tables II.7.26 and II.7.27. Revised or newly added emission factors are highlighted in red. Detailed information on the derivation of these emission factors can be found in Annex 49.

Table II.7.26 PCDD/PCDF emission factors for source category 7f Petroleum Refining (flaring of gases)

7f	**Petroleum Refining (flares)**	**EF_{Air} µg TEQ/TJ fuel burned**
	Classification	
1	Flares	**0.25**

Table II.7.27 PCDD/PCDF emission factors for source category 7f Petroleum Refining (production processes)

7f	Petroleum Refining (production processes)	Emission Factors				
	Classification	Air µg TEQ/t oil[A]	Water pg TEQ/L	Land	Product	Residue µg TEQ/t residue
1	Catalytic reforming unit (including catalyst regenerator)	**0.017**	NA	NA	NA	**14**
2	Coking unit	**0.41**	NA	NA	NA	ND
3	Refinery-wide wastewater treatment	ND	**5**	ND	ND	ND

[A] Mass of oil specific to each processing unit

Level of confidence

Emission factors for this source category are associated with a medium level of confidence for all classes, as they are based on a low data range, but not based on expert judgment, and are derived based on a limited geographical coverage.

7g Textile Production

The textile industry is one of the longest and most complicated industrial chains in the manufacturing sector. It is a diverse, fragmented group of establishments that produce and/or process textile-related products, such as fiber, yarn, and fabric, for further processing into finished goods. These establishments range from small "back street" operations with few controls to large-scale highly sophisticated industrial operations with comprehensive pollution controls. Because the processes for converting raw fibers into finished products are complex, most textile mills specialize (USEPA 1997b).

Textile production industries are potential sources of PCDD/PCDF due to a number of factors:

- Raw materials may be contaminated with PCDD/PCDF due to treatment with PCDD/PCDF-contaminated pesticides, such as pentachlorophenol;
- Dyes and pigments used on fibers and textiles may be contaminated with PCDD/PCDF, for example, dioxazine dyes produced from chloranil and phthalocyanine-based pigments;
- Finishing processes may include the use of PCDD/PCDF-contaminated chemicals, such as Triclosan, an antimicrobial agent;
- Boilers and heaters may be used for power and heat generation (see Source Group 3);
- Incinerators may be used for disposal of process residues;
- Large volumes of effluent water are released into the environment.
- Formation of PCDD/PCDF during finishing (Križanec *et al*. 2005).

Details on textile production processes are presented in the BAT&BEP Guidance.

Emission Factors

PCDD/PCDF have been detected in air emissions, wastewater and wastewater treatment sludge from textile mills. However, currently available data are not sufficient to support the derivation of emission factors for these vectors. PCDD/PCDF emission factors for two source classes of products are listed in Table II.7.28. The derivation of these emission factors as well as discussion of existing information on releases to air, water and wastewater treatment sludge are addressed in Annex 50.

Table II.7.28 PCDD/PCDF emission factors for source category 7g Textile Production

7g	Textile Production	Emission Factors (µg TEQ/t textile)				
	Classification	**Air**	**Water**	**Land**	**Product**	**Residue**
1	Low-end technology	ND	ND	ND	100	ND
2	Mid-range, non-BAT technology[A]	ND	ND	ND	0.1	ND
3	High-end, BAT technology	NA	NA	NA	NA	NA

[A] Textile technology that does not involve either formation of PCDD/PCDF or transfer from another vector.

Level of confidence

Emission factors for this source category are associated with a low level of confidence for all classes, due to scarcity and lack of representativeness of data.

7h Leather refining

The tannery operation consists of converting the raw skin or hide of an animal into leather for use in the manufacture of a wide range of products. This involves a sequence of complex chemical reactions and mechanical processes. Amongst these, tanning is the fundamental stage, which gives leather its stability and essential character. The tanning industry is a potentially pollution-intensive industry with environmental concerns that include air emissions, wastewater, and solid waste.

PCDD/PCDF have been detected in finished leather goods. Evidence suggests that the sources of PCDD/PCDF are contaminated dyes, such as those derived from chloranil, and contaminated biocides, such as PCP. While leather production processes have not been evaluated for PCDD/PCDF formation or occurrence, the use of PCDD/PCDF-contaminated dyes and biocides chemicals can be expected to result in the occurrence of PCDD/PCDF in process wastewater and sludges from wastewater treatment. Also, new formation of PCDD/PCDF may occur in the leather production chain where process wastewater is treated and where wastewater treatment sludge and other process wastes are incinerated.

Leather production processes are described in greater detail in Annex 51 and in the BAT&BEP Guidelines.

Emission Factors

Emission factors for PCDD/PCDF releases to air, water, land, and residues could not be derived due to lack of information. However, the quantities, methods of treatment, and fate of wastewater, treated wastewater effluents, wastewater treatment sludge, and other solid wastes should be noted to the extent possible since releases to water and residues could be high. If wastewater treatment sludge and/or other wastes are incinerated or otherwise combusted, this should also be noted since release to air and in residues could be high.

Emission factors for release to products are given in Table II.7.29. The derivation of these emission factors is addressed in Annex 51.

Table II.7.29 PCDD/PCDF emission factors for source category 7h Leather Refining

7h	**Leather Refining**	**Emission Factors (µg TEQ/t leather)**				
	Classification	**Air**	**Water**	**Land**	**Product**	**Residue**
1	Low-end technology	ND	ND	ND	1,000	ND
2	Mid-range technology	ND	ND	ND	10	ND

Level of confidence

Emission factors for this source category are associated with a low level of confidence for all classes, due to scarcity and lack of representativeness of data.

8 – Miscellaneous

This category comprises five processes, shown in Table II.8.1, that were not placed in other source groups for various reasons. For example, two of the processes – drying of green fodder and smoke houses – are included here even though they are combustion processes that might be considered to be similar to processes addressed in source category 1f Waste wood combustion or source category 3d Household heating and cooking. These are shown in Table II.8.1.

Table II.8.1 Overview of source categories included in group 8 – Miscellaneous

8 – Miscellaneous		**Potential release route**				
	Source categories	**Air**	**Water**	**Land**	**Product**	**Residue**
a	Drying of Biomass	x			x	x
b	Crematoria	x				X
c	Smoke houses	x			x	X
d	Dry cleaning		x		x	x
e	Tobacco smoking	x				x

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

Table II.8.2 Relevance to Article 5, Annex C of the Stockholm Convention

No	**Toolkit source category**	**Part II**	**Part III**	**Relevant source category in Annex C**
8b	Crematoria		X	Crematoria

An example of elaborating source inventory and release estimate for this source group is included in the example inventory 9.

8a Drying of Biomass

Drying of woody or herbaceous biomass, *e.g*. wood chips or green fodder, occurs either with or without containment, in which the combustion gases contaminated with unintentional POPs enter in contact with the material being dried.

Other processes that use direct heating methods (e.g. for foodstuffs) should be addressed under source category 8c smoke houses. Processes without contact should be addressed in Source Group 3 Power Generation and Heating.

Under controlled conditions, clean fuels such as wood are used. The drying of green fodder using poor fuels, *e.g.*, treated wood, used textiles, carpets, etc., may lead to PCDD/PCDF formation and contamination of the fodder. For example, in 2005, in Germany, it was shown that the use of contaminated wood as fuel had resulted in very high concentrations of PCDD/PCDF in the fodder. When such contaminated fodder is fed to livestock, PCDD/PCDF can be transferred to the human food chain.

Emission Factors

PCDD/PCDF emission factors for three source classes are listed in Table II.8.3. Revised or newly added emission factors are highlighted in red. Detailed information on how these emission factors have been derived can be found in Annex 52.

Guidance for classification of sources

Class 1 is applied when using highly contaminated fuel (PCP- or otherwise treated material).

Class 2 is applied when using moderately contaminated fuel.

Class 3 is applied when using clean fuel.

Table II.8.3 PCDD/PCDF emission factors for source category 8a Drying of Biomass

8a	**Drying of Biomass**	**Emission Factors (µg TEQ/t dry product)**				**Concentration (µg TEQ/t ash)**
	Classification	**Air**	**Water**	**Land**	**Product**	**Residue**
1	Highly contaminated fuel (PCP- or otherwise treated material)	10	NA	ND	0.5	**2000**
2	Moderately contaminated fuel	0.1	NA	ND	0.1	**20**
3	Clean fuel	**0.01**	NA	ND	0.1*	**5**

* For herbaceous biomass being dried, use an $EF_{Product}$ of 1 µg TEQ/t dry product

Activity rates

- Agricultural institutions or feedingstuff producers;
- National statistics on energy sources;
- Surveys addressed to biomass producers.

Level of confidence

The emission factors for this source category have been assigned a low level of confidence based on the scarcity of data and limited accessibility of activity information. Expert judgment has also been used in deriving these emission factors.

8b Crematoria

Cremation, reducing human bodies to ashes by burning, is a common practice in many societies. The essential components for cremation are the coffin (and the corpse), the main combustion chamber, and where applicable the afterburning chamber and air pollution control system. The cremation process is described in detail in the BAT&BEP Guidelines. The Guidelines equally provide information on PCDD/PCDF emissions from this process.

Emission Factors

PCDD/PCDF emission factors for three source classes are listed in Table II.8.4. Detailed information on how these emission factors have been derived can be found in Annex 52.

Guidance for classification of sources

Class 1 includes facilities with only one burner, small combustion chamber, poor combustion conditions, *e.g.*, temperatures below 850°C, uncontrolled combustion air flow, etc., if plastic or other decoration materials are burned together with the coffin, if the wood of the coffin has been treated with wood preservatives, or if there is no flue gas cleaning system in place.

Class 2 includes facilities where the combustion conditions are better – temperatures securely above 850°C, controlled combustion air flow, no plastics or other problematic input materials - and some dust removal is in place. This class also includes open air cremations.

<u>Class 3</u> includes state-of-the-art facilities with sophisticated air pollution control systems.

Table II.8.4 PCDD/PCDF emission factors for source category 8b Crematoria

8b	**Crematoria**	**Emission Factors (µg TEQ per cremation)**				
	Classification	**Air**	**Water**	**Land**	**Product**	**Residue**
1	No control	90	NA	NA	NA	ND
2	Medium control or open air cremations	10	NA	NA	NA	2.5
3	Optimal control	0.4	NA	NA	NA	2.5

Activity rates

- Operators of crematoria (via questionnaires) in case of few large crematoria in the country;
- National statistics on number of deceased per year and expert judgment with regards to the percentage of cremation;
- Centralized data collection on federal or provincial government level.

Level of confidence

Class 1 emission factors are assigned a low level of confidence due to the low stability of the process, and only a limited number of measurements being available. Class 2 emission factors are assigned a medium level of confidence due to the larger range of the data. Finally, Class 3 emission factors are assigned a high level of confidence due to availability of consistent datasets from measurements with high geographical coverage.

8c Smoke Houses

Smoking food for preservation of meat and fish is a common practice in many countries. Smoke houses are commonly small installations that use wood as fuel and have sub-optimal combustion conditions.

Emission Factors

PCDD/PCDF emission factors for three source classes are listed in Table II.8.5. For smoking foodstuffs in open air, use the EF_{Air} from source category 3d, class 5 (open fire three stone stoves). Detailed information on how these emission factors have been derived can be found in Annex 52.

Guidance for classification of sources

<u>Class 1</u> should be applied if treated wood or other contaminated biomass is used as fuel.

<u>Class 2</u> should be used if clean wood or other biomass is used as fuel.

<u>Class 3</u> should be applied if clean wood or other biomass is used as fuel and there is a state-of-the-art air pollution control system in operation.

Table II.8.5 PCDD/PCDF emission factors for source category 8c Smoke Houses

8c	**Smoke Houses**	**Emission Factors (µg TEQ/t product)**				**Concentration (ng TEQ/kg ash)**
	Classification	**Air**	**Water**	**Land**	**Product**	**Residue**
1	Contaminated fuels	50	NA	NA	ND	2,000

2	Clean fuels, no afterburner	6	NA	NA	ND	20
3	Clean fuels, afterburner	0.6	NA	NA	ND	20

Activity rates

- National statistics;
- Local producers of smoked foodstuffs;
- Surveys sent to/interviews with local producers.

Level of confidence

The emission factors for this source category have been assigned a low level of confidence based on the scarcity of available data. Expert judgment has also been used in deriving these emission factors.

8d Dry Cleaning

PCDD/PCDF have been detected in the distillation residues from dry cleaning (cleaning of textiles with organic solvents, not washing with water). The PCDD/PCDF sources have been identified as the use of contaminated biocides, such as PCP, to protect textiles or raw materials – wool, cotton, etc. – and the use on textiles of PCDD/PCDF-contaminated dyes and pigments. The dry cleaning process itself does not generate PCDD/PCDF, but rather redistributes PCDD/PCDF already present in the textiles via prior contamination.

During the dry cleaning process, PCDD/PCDF are extracted from the textiles and transferred into the cleaning solvent. When the solvent is distilled for recovery and reuse, PCDD/PCDF are concentrated in distillation residues, which normally are disposed of. Detailed research has shown that PCDD/PCDF concentrations in the distillation residues do not depend on the solvent present in the dry cleaning process (Fuchs *et al*. 1990, Towara *et al*. 1992). Therefore, the influence of the solvent used is negligible; typical solvents are perchloroethylene, petrol, or fluorocarbons.

Emission Factors

PCDD/PCDF emission factors for two source classes are listed in Table II.8.6. Detailed information on the derivation of these emission factors can be found in Annex 52.

Guidance for classification of sources

Class 1 includes dry cleaning of highly contaminated textiles, *e.g*. carpets or heavy curtains suspected to be treated with PCP (the country of origin may be an indicator) or clothing of workers or other textiles from dioxin-polluted environments.

Class 2 includes cleaning of uncontaminated clothing and other textiles.

Table II.8.6 PCDD/PCDF emission factors for source category 8d Dry Cleaning

8d	**Dry Cleaning**	**Emission Factors (in µg TEQ/t)**				**Concentration in distillation residue (µg TEQ/t)**
	Classification	**Air**	**Water**	**Land**	**Product**	**Residue**
1	Heavy textiles, PCP-treated, etc.	NA	NA	NA	NA	3,000
2	Normal textiles	NA	NA	NA	NA	50

Activity rates

As an indication, 15g of residues are formed per kilogram of treated clothes (data from the French Technical Center on Cleaning - CTTN). Activity data can be retrieved from competent authorities that license the dry cleaning shops, and waste collectors.

Level of confidence

The emission factors for this source category have been assigned a low level of confidence due to changes and complexity in the textile and leather manufacturing.

8e Tobacco Smoking

As any other thermal process, "combustion" of cigarettes and cigars produces PCDD/PCDF. The quantity of tobacco in cigarettes varies but is commonly less than 1 gram per cigarette. Cigars vary both in their size and their tobacco load. Large cigars may contain as much tobacco as an entire pack of 20 cigarettes, while small cigars (cigarillos) may be similar in size and tobacco content to that of one cigarette.

Emission Factors

PCDD/PCDF emission factors for two source classes are listed in Table II.8.7. Revised or newly added emission factors are highlighted in red. Detailed information on how these emission factors have been derived can be found in Annex 52.

Guidance for classification of sources

Class 1 should be applied to cigar smoking.

Class 2 applies to cigarette smoking.

Table II.8.7 PCDD/PCDF emission factors for source category 8e Tobacco Smoking

8e	**Tobacco Smoking**	**Emission Factors (µg TEQ/million cigars or cigarettes)**				
	Classification	**Air**	**Water**	**Land**	**Product**	**Residue**
1	Cigar	0.3	NA	NA	NA	**0.3**
2	Cigarette	0.1	NA	NA	NA	**0.1**

NB: The emission factors for tobacco smoking are applied to total cigarette/cigar numbers, not to the weight of tobacco.

Activity rates

The activity rate can be assessed by the following mass-balance equation: Production - Export + Import. While cigarette data are available as numbers of cigarettes, loose tobacco and cigars are usually reported in weight. A conversion factor of 1 g of tobacco per cigarette may be used to estimate the number of cigarettes, *i.e.* 1 ton of loose tobacco is equivalent to 1,000,000 cigarettes.

Level of confidence

The level of confidence assigned to these emission factors is low due to limited data available and difficult experimental design.

9 – Disposal / Landfill

Non-thermal waste disposal processes are addressed in this source group. Except in certain cases, these processes are only routes of PCDD/PCDF release, not sources of PCDD/PCDF formation and release. PCDD/PCDF that are already present in the wastes being treated become concentrated or released to one or more vectors by these treatment and disposal processes (see Table II.9.1).

These processes are used to dispose of PCDD/PCDF-contaminated wastes, many of which are residues of processes that have been addressed in other source groups. The management of these residues, *e.g*. physical, biological, chemical, or thermal treatment or containment in secure landfills, burial in dumps and pits, spreading on land, or direct discharge of untreated effluents into rivers, lakes or oceans, can result in PCDD/PCDF releases to the environment.

The fate of PCDD/PCDF-containing residues should be well-documented, because of the potential for mismanagement to result in increased and widespread exposure in humans and domestic animals. As an example, the Belgian chicken incident originated in a small volume of used PCB oil (contaminated with PCDF) being introduced into fat subsequently used for producing feedstuff for domestic animals (EU SCAN 2000).

Table II.9.1 Overview of source categories included in group 9 – Disposal / Landfill

9 – Disposal / Landfill		**Potential release vector**				
	Source categories	**Air**	**Water**	**Land**	**Product**	**Residue**
a	Landfills, Waste Dumps and Landfill Mining		x	X		
b	Sewage/sewage treatment	(x)	x	x	x	x
c	Open water dumping		x	X*		
d	Composting			x	x	
e	Waste oil treatment (non-thermal)	x	x	x	x	x

* Sediment in creeks, rivers, estuaries and oceans.

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

Table II.9.2 Relevance to Article 5, Annex C of the Stockholm Convention

No	**Toolkit source category**	**Part II**	**Part III**	**Relevant source category in Annex C**
9e	Waste oil treatment (non-thermal)		X	Waste oil refineries

An example of elaborating a source inventory and release estimate for this source group is included in the example inventory 10.

9a Landfills, Waste Dumps and Landfill Mining

Landfills and waste dumps are sites where waste is buried in engineered landfills and unlined pits or deposited in surface piles (open dumps). An engineered landfill is a constructed waste storage site where the wastes are contained and controlled by liners and caps. In contrast, pits, dumps and piles have no engineered containment or pollution control techniques and are largely unregulated and uncontrolled.

In landfills and dumps, biodegradable wastes decompose with the formation of gases (with methane as a major constituent when the degradation proceeds anaerobically) and leachate. The passage of rain and other water through the waste in landfills and dumps generates contaminated leachate and runoff. Where no collection systems are installed, landfill gases and leachate escape from the dump in an uncontrolled manner. While PCDD/PCDF have not been quantified/reported in landfill gases, they are known to occur in landfill leachate or seepage and, in some cases, nearby soils.

Combustion of landfill gases in flares and other devices is addressed in source category 3c and releases due to open burning of waste at landfills and dumps are addressed in source category 6b.

Landfill mining

A large amount of PCDD/PCDF and other unintentional POPs have been deposited over the last century in landfills and dumpsites, with the largest reservoirs stemming from chlorine and organochlorine production (see Source Group 10). Landfill mining and reclamation, or excavation/remediation of landfills is a process whereby solid wastes which have previously been landfilled are excavated and processed.

The objectives of landfill mining/reclamation and excavation/remediation can be threefold:

- Recovery of land and landfill space
- Recovery of materials
- Environmental protection and remediation

As an example, PCDD/PCDF contaminated lime has been mined from a landfill containing residues from VCM/EDC production (Torres *et al*. 2012). This contaminated lime was partially used for neutralization of citrus pulp which was subsequently used as feedstuff for cattle in Europe. This resulted in contamination of milk and dairy products in several European countries (Torres *et al*. 2012, Malisch 2000; see example inventory 10).

The excavation of landfills for remediation purposes reduces or prevents releases of more water soluble compounds contaminating groundwater, surface water or drinking water. Excavation can also be undertaken due to long term cost considerations and to avoid burdening future generations.

The quantity of PCDD/PCDF in landfills being excavated is site specific and needs to be individually assessed in each case (Forter 2006, Torres *et al*. 2012, Weber *et al*. 2008). The excavation and remediation activities of landfills containing wastes from organochlorine industries or other wastes highly contaminated with PCDD/PCDF must also consider the risks of occupational exposure to PCDD/PCDF. The excavated wastes need to be treated in an environmentally sound manner as described in the BAT&BEP Guidelines.

Emission Factors

PCDD/PCDF emission factors for three source classes are listed in Table II.9.3. Revised or newly added emission factors are highlighted in red. Detailed information on how these emission factors have been derived can be found in Annex 53.

Guidance for classification of sources

Class 1 applies to landfills where wastes from source groups 1 to 8 are deposited.

Class 2 applies to landfilling of waste which may contain some hazardous components. A typical situation is in cases when no waste management is in place.

Class 3 applies to landfilling of non-hazardous wastes.

When assessing releases from this source category, care should be taken that no double counting occurs. This category covers wastes generated at national level that are landfilled. It does not include municipal or hazardous waste that is accounted for in other source groups or source categories, especially in:

- Source Group 1: 1a Incineration of municipal solid waste, 1b Incineration of hazardous waste and 1c Medical waste incineration;
- Source Group 6: classes 6b1 Fires at waste dumps or 6b3 Open burning of domestic waste;
- Source Group 3: class 4c1 Production of bricks using contaminated fuels or similar high temperature production processes using waste fuels.

Table II.9.3 PCDD/PCDF emission factors for source category 9a Landfills, Waste Dumps and Landfill Mining

9a	**Landfills and Waste Dumps**	**Emission Factors (µg TEQ/t waste disposed of)**				
	Classification	**Air**	**Water**	**Land**	**Product**	**Residue**
1	Hazardous wastes	**NA**	**5**	**NA**	**NA**	**NA***
2	Mixed wastes	**NA**	**0.5**	**NA**	**NA**	**50**
3	Domestic wastes	**NA**	**0.05**	**NA**	**NA**	**5**

*The residues of wastes from category 1 to 8 are accounted in the respective categories.

Activity rates

Activity rates might be available on national level and on municipality level. In general there historical data are scarce. Additionally, the set of data for PCDD/PCDF in waste are uncertain because of the small regional coverage of these data.

Level of Confidence

There are multiple sources of uncertainty associated with the PCDD/PCDF levels in waste and the emissions from landfills. Emission factors are thus assigned a medium to low level of confidence.

9b Sewage and Sewage Treatment

Sewage is waste that is dissolved and/or suspended in water. Sewage, also called wastewater, typically includes human feces and urine, bathwater, water used in washing clothes and other items, and, in some cases, storm water run-off and industrial wastewater.

This category addresses municipal sewage that is collected and transported to sewage treatment facilities. Untreated sewage that is collected and discharged directly to surface water, such as rivers, lakes and oceans, is addressed in source category 9c Open Water Dumping. Wastewater and wastewater treatment from industrial production is addressed in Source Group 7 – Production and Use of Chemicals and Consumer Goods.

Sewage treatment ranges from simple removal of large solids by coarse screening to further solids removal in settling ponds, biological and chemical treatment, disinfection, reverse osmosis filtration and other advanced technologies. These commonly used sewage treatment methods produce an aqueous effluent and a solid residue, sewage sludge. PCDD/PCDF concentrations in treated effluent are ordinarily low. However, when chlorine is used to disinfect treated effluent, PCDD/PCDF concentrations can increase, in some cases, by as much as 50-fold (Pujadas *et al*. 2001). Most of the PCDD/PCDF found in sewage and, subsequently, in treated effluent and sewage sludge originate in other processes or products.[12] For example, PCDD/PCDF may occur in sewage because they have been washed from clothing and other textiles treated with PCDD/PCDF-contaminated biocides or dyes and pigments (see source category 7d), due to the entry into sewers of runoff of atmospheric deposition of PCDD/PCDF from combustion sources (Gihr *et al*. 1991), or due to discharges into sewers of untreated industrial wastewater.

For many years, PCDD/PCDF have been reported in sewage sludge of many countries (Clarke *et al*. 2008). Decreasing trends have been reported in countries such as Germany and Austria, as well as in Spain (Martinez *et al*. 2007, De la Torre *et al*. 2011). The management of sludge can also result in releases of PCDD/PCDF. For example, land application of sludge can lead to increased PCDD/PCDF in soils (Molina *et al*. 2000, Rideout and Teschke 2004), in certain vegetation grown on sludge-treated soils (Engwall and Hjelm 2000), and in the tissues and other products of animals that forage on PCDD/PCDF-contaminated soils (Schuler *et al*. 1997, Rideout and Teschke 2004). Likewise, sludge buried in landfills may contribute to PCDD/PCDF in landfill leachates (De la Torre *et al*. 2011).

Untreated sewage from remote, undeveloped and non-industrialized areas is expected to have relatively low PCDD/PCDF concentrations. Low concentrations may be also expected in countries with stringent controls on discharges of industrial wastewater to sewers, effective controls on the use of PCP, other biocides and dyes and pigments on textiles, and bans on the use of chlorine-bleached toilet paper. Higher levels can be expected in urban areas with mixed industry and use of PCDD/PCDF-contaminated consumer goods. Discharges of untreated industrial wastewater to public sewers can cause very high levels of PCDD/PCDF in sewage sludge (for reference, see Group 7 Production and Use of Chemicals and Consumer Goods).

With more advanced treatment – such as biological and chemical treatment - most PCDD/PCDF are likely to be concentrated in the sludge. The amount of PCDD/PCDF in the effluent is likely to be influenced by the amount of suspended solids remaining in the effluent.

Emission Factors

PCDD/PCDF emission factors for three source classes are listed in Table II.9.4. Revised or newly added emission factors are highlighted in red. Detailed information on how these emission factors have been derived can be found in Annex 53.

Guidance for classification of sources

Class 1 should be applied where, besides normal domestic effluents, industrial effluents with a potential to contain PCDD/PCDF as described for categories 1 to 8 are collected in the same sewer system.

Class 2 should be applied for urban, industrial areas without specific potential to contain PCDD/PCDF.

Class 3 should be applied to remote areas with no known PCDD/PCDF sources and urban areas with only domestic inputs.

Table II.9.4 PCDD/PCDF emission factors for source category 9b Sewage and Sewage Treatment

9b	Sewage and Sewage Treatment	Emission factors

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[12] Biogenic formation of PCDD/PCDF from dioxin precursors like chlorophenols has been reported in sewage sludge by some authors. However, biological transformation cannot be quantified in terms of emission factors. Since the use of chlorophenol (including PCP) has decreased the last decades, this source can be considered as not relevant. PCDD/PCDF may also be produced where sludge is thermally dried.

	Classification	Air	Water (pg TEQ/L)	Land*	Product = Residue (µg TEQ/t d.m.)
1	Mixed domestic and specific industrial inputs**	NA NA	**10**[a] **1**[b]		**NA**[a] **200**[b]
2	Urban and industrial inputs	NA NA	**1**[a] **0.2**[b]		**NA**[a] **20**[b]
3	Domestic inputs	NA NA	**0.04**[a] **0.04**[b]		**NA**[a] **4**[b]

[a]no sludge removal, [b]with sludge removal

*Use $EF_{Product}$ when residue (sludge) is applied to land.

** for those emissions which are not covered in source group 7.

Note: the emission factors are given in pg TEQ/L of treated effluent and in µg TEQ per ton of sewage sludge (dry matter = d.m.) generated.

Activity rates

Activity rates on production of sewage sludge might be available on national level and on municipality level. One challenge is to assign which facilities to classify as class 1 with specific industrial input. A national survey for PCDD/PCDF in sewage sludge is helpful to facilitate source classification. A regular survey for sewage sludge is not recommended or might be performed every 5 or 10 years. For facilities with elevated levels (above 30 ng TEQ/kg), source(s) might be traced, and measures for release reduction introduced.

Level of Confidence

The emission factor values are assigned a high confidence level, based on the geographic coverage of available datasets and consistency among the results of the various studies.

9c Open Water Dumping

Open water dumping is the practice of discharging untreated wastewater or other wastes directly into surface waters, *i.e.* rivers, ground water, lakes or oceans.

Emission Factors

PCDD/PCDF emission factors for three source classes are listed in Table II.9.5.

Guidance for classification of sources

Class 1 should be applied if the wastewater being discharged includes both domestic and industrial wastewater with a potential to contain PCDD/PCDF as described for source group 1 to 8 or storm water runoff from urban, peri-urban or industrialized areas.

Class 2 should be applied for urban and peri-urban areas with little or no industries.

Class 3 includes remote areas with no known PCDD/PCDF sources.

Table II.9.5 PCDD/PCDF emission factors for source category 9c Open Water Dumping

9c	Open Water Dumping	Emission Factors (µg TEQ/m^3)				
	Classification	Air	Water	Land	Product	Residue

1	Mixed domestic and industrial wastewater	NA	0.005	NA	NA	NA
2	Urban and peri-urban wastewater with little or no industrial input	NA	0.0002	NA	NA	NA
3	Remote environments	NA	0.0001	NA	NA	NA

9d Composting

Composting is the biological decomposition of biodegradable solid waste under controlled predominantly aerobic conditions to a state that is sufficiently stable for nuisance-free storage and handling and is satisfactorily matured for safe use in agriculture (Diaz *et al*. 2005). Feedstocks for composting include a wide variety of materials, *e.g*., kitchen and garden waste, sewage sludge, agricultural crop residues, some industrial wastes, animal manures and human excreta.

PCDD/PCDF values in compost in Europe were between 3 and 12 ng TEQ/kg (Brändli *et al*. 2005, 2008). In Brazil, organic composts (separated at source) had an average PCDD/PCDF content of 14 ng TEQ/kg (Grossi *et al*. 1998). However, composts produced from mixed waste where organic fractions have been separated after collection (“grey compost”) had an average of 57 ng TEQ/kg, with a maximum of 150 ng TEQ/kg in metropolitan areas, and an average of 27 ng TEQ/kg in small towns (Grossi *et al*. 1998). Compost impacted from pulp and paper sludge using Kraft process also had high values (99 ng TEQ/kg). These “grey” composts with levels of 50 ng TEQ/kg and higher are not considered suitable for agriculture or horticulture in Europe. However, standards differ among other regions and countries.

Emission Factors

PCDD/PCDF emission factors for two source classes are listed in Table II.9.6. Revised or newly added emission factors are highlighted in red. Detailed information on how these emission factors have been derived can be found in Annex 53.

Guidance for classification of sources

Class 1 should be applied when the organic fraction is separated from mixed wastes and then composted. Such composts also contain higher levels of heavy metals and plastics.

Class 2 should be applied for compost where organics (kitchen/market waste, vegetables/fruit etc.) have been separated at source or green materials have been used.

Table II.9.6 PCDD/PCDF emission factors for source category 9d Composting

9d	**Composting**	**Emission Factors (µg TEQ/t d.m.)**				
	Classification	**Air**	**Water**	**Land***	**Product**	**Residue**
1	Compost of organic wastes separated from mixed wastes	NA	NA	NA	**50**	NA
2	Clean compost (organic wastes separated at source or green material)	NA	NA	NA	**5**	NA

*Compost is finally applied to land

Activity rates

Activity rates on production of compost might be available on national level and on municipality level. The activity rates of composting on household level might not be available from national statistics but might need a survey or an expert judgment.

Level of Confidence

The emission factor values have been assigned a high level of confidence. Nevertheless, uncertainties exist where organic industrial residues are used (*e.g*. from pulp and paper industry).

9e Waste Oil Treatment (Non-thermal)

The estimate of PCDD/PCDF releases from waste oil treatment is difficult for several reasons. Firstly, there is no clear definition of “used” oil or “waste” oil. For the purpose of the Toolkit, waste oils (or used oils) are defined as any petroleum-based, synthetic, or plant- or animal-based oil that has been used. Waste oils may originate from two large sources: used industrial oils, and vegetable or animal waste oils. Among the industrial waste oils, three main oil streams can be identified: industrial oil (for example, hydraulic oil, engine lubricant, cutting oil); garage or workshop oil; and transformer oil. More information can be found in the BAT&BEP Guidelines.

Waste oils have been found to be contaminated with PCDD/PCDF and PCB. PCB-containing oils from transformers are addressed in source category 10f.

At present there is no evidence that PCDD/PCDF or PCB are newly formed in waste oil refineries. The data available indicate that PCDD/PCDF and PCB released from waste oil refineries or waste oil handling and management plants are from the industrial, intentional production of PCB or chlorobenzenes that are present in waste oils either by contamination in the synthesis process (of these chemicals) or have become contaminated during the use phase or earlier recycling processes. More information can be found in the BAT&BEP Guidelines.

Waste oil collected in countries will end up in other processes and has to be included in the categories on waste incineration (1a and 1b), power plants (3a), domestic heating and cooking (3e), cement kilns (4a), brickworks (4c), asphalt mixing stations (4f), or transportation (5d).

The management of PCDD/PCDF or PCB contaminated oil may result in human exposure of the personnel collecting or otherwise handling the oils. During storage and handling, diffuse emissions may occur. Contamination of the environment may also result from spills. Residues from recycling operations may contain high concentrations of PCDD/PCDF. Improper disposal may result in contamination of land or water. It can be assumed that a site- or process-specific evaluation has to be performed.

Presently, no emission factors can be given with respect to any of the release vectors.

10 – Contaminated Sites and Hotspots

Article 6 of the Stockholm Convention encourages parties to develop strategies to identify sites contaminated with unintentional POPs. This source group includes an indicative list of activities that might have resulted in the contamination of soils and sediments with PCDD/PCDF and other unintentional POPs, including related deposits.

PCDD/PCDF from reservoirs including contaminated sites and hotspots represent nowadays an important source of human exposure, often through food contamination: recent accidents involving food and animal feedstuff in Europe have been caused by historic PCDD/PCDF contamination from past production of chlorinated organics and contaminated sites (Fiedler *et al*. 2000b, Torres *et al*. 2012, Weber *et al*. 2008a,b) highlighting that PCDD/PCDF are released from these sources into the food chain.

The procedure comprises three tasks:

I. Identifying historical activities that could have caused contamination and identifying the potentially contaminated sites;
II. Assessing these sites for the likely magnitude of the contamination and ranking by their exposure risk;
III. Assessing the degree of contamination of the most significant sites by detailed analysis.

Steps for identification, ranking and detailed assessment of the sites

I. Identifying potentially contaminated sites

A wide variety of PCDD/PCDF sources exists worldwide, which has likely resulted in a large number of (potentially) contaminated sites through historic releases. The Toolkit shows that the strength of the various PCDD/PCDF sources varies by several orders of magnitude. Therefore, a prioritization of contaminated sites from historic sources needs to consider the total amount of PCDD/PCDF that was likely produced from the respective sources, the related management schemes and former destruction efforts. Often, details on the management of historic releases are not known, therefore a tiered approach is needed to inventory and categorize sites.

The largest amounts of PCDD/PCDF and other unintentional POPs were generated in the production processes of organochlorine chemicals, in particular of PCDD/PCDF precursors such as chlorophenols, PCB or other chlorinated aromatic compounds. Tens to hundreds of kg TEQ of historic deposits have been documented for single factories (Götz *et al*. 2012, Verta *et al*. 2010, Forter 2006); amounts of the same order of magnitude were recorded for single hotspot sites (Götz *et al*. 2012). The same is true for unintentionally produced HCB, where single factories have disposed of HCB wastes in the order of 10,000 tons (Weber *et al*. 2011b, Vijgen *et al*. 2011).

The following source groups should be considered when setting priorities for establishing inventories and assessing sites potentially contaminated with PCDD/PCDF and other unintentional POPs, as well as (historic) stockpiles of contaminated wastes[13]:

- Production of chlorine (in particular chlor-alkali processes having used graphite electrodes).

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[13] The list is established according to the life cycle of chlorine and organochlorine compounds.

- Production sites of PCDD/PCDF precursors (*e.g*. chlorophenols, chlorinated pesticides, PCB) or HCB precursors (*e.g*. perchlorethene, trichloroethene, tetrachlormethane) and related waste deposits.

- Factories having used elemental chlorine in production processes (*e.g*. magnesium production, or pulp and paper production) with high PCDD/PCDF releases often in solids/sludges or to water, including related contaminated sediments.

- Use or application sites of organochlorine compounds known to contain PCDD/PCDF or having PCDD/PCDF precursor potential (production sites of PCB-filled equipment, PCP use in wood preservation, application areas of pesticides containing PCDD/PCDF).

- End-of-life storage and disposal/dumping sites of organochlorine compounds known to contain PCDD/PCDF or having PCDD/PCDF precursor potential (obsolete pesticide storage/burial, PCB storage).

- Thermal sources with high historic releases of PCDD/PCDF to air, water or wastes and related contamination.

- Accidents including fires with liquids and other materials polluted with PCDD/PCDF (often taking place at sources mentioned above).

Monitoring data are rarely available before the development of an inventory. A listing of contaminated sites is therefore prepared based only on information on historic activities having likely resulted in high releases of PCDD/PCDF and other unintentional POPs over the last century. Consequently, in the initial stage of inventory development, the sites related to the above listed high priority activities can be categorized without a detailed assessment as “potentially polluted sites”. Using this simple approach (Tier 1), a wide range of “potentially polluted sites” can initially be listed. Often, in this stage, only the factories and areas surrounding the known or suspected sources can be identified as “potentially polluted”, without knowing details on *e.g*. deposits, polluted soil or sediments. These sites will be included in a list or a database of contaminated sites, noting that further investigations are needed.

II. Ranking the contaminated sites

In the second phase (Tier 2), these “potentially polluted sites” are subject to further assessment of historic production, and evaluation of quantities of chemicals produced, waste generation and management, thermal processes used for destruction or releases and historic release vectors. In this tier 2 assessment, the detailed location of potentially contaminated sites is assessed, in particular production sites, related landfills and dump sites, rivers and lakes having received releases, and areas where air releases have been deposited. These sites can be identified as “likely contaminated sites” or “contaminated sites”, depending on PCDD/PCDF contamination levels. Such data might be documented in archives of the respective companies or competent authorities responsible for factory inspection/audits. In addition, data from factories with similar production or technologies may be used for a first semi-quantitative estimate. Tier 2 might already include a first screening of PCDD/PCDF contamination at suspected sites with high human exposure risk to assess/confirm PCDD/PCDF pollution and facilitate appropriate action. Based on the compilation of this information, the site can be listed in the inventory as a (likely) polluted site, and the need for a further detailed assessment should be noted. Already at this stage, the site might be classified as a high priority site or as a site with lower priority. Depending on the priority classification, the respective competent authority and the owner of the site are informed of the necessary steps for further detailed assessment of pollution (Tier 3) and the urgency of such assessment. A preliminary risk assessment for each site/hotspot should be made in order to establish the necessary national priorities, so that in case of limited available budgets, the most urgent sites can be selected and dealt with accordingly.

III. Detailed assessment of the most significant contaminated sites

In the third phase (Tier 3), a detailed assessment of the site is conducted including field measurements to assess the extent of contamination in soils, sediments and possibly ground and surface water (for the more water-soluble unintentional POPs). This assessment also includes an evaluation of potential releases and human exposure via all relevant pathways. Detailed records of the location of the sites should be compiled *e.g.* places where the potentially contaminating operations took place and where associated wastes have been disposed of, ideally using geospatial data. The current use of the site and any associated human exposure risks should also be assessed and recorded. A detailed risk assessment and a conceptual site model might also be developed at this stage.

Details on assessing POPs contaminated sites have been compiled in the following documents and are not further described:

a) UNIDO "*POP contaminated site investigation and management toolkit*", which aims at assisting developing countries in the identification, classification and prioritization of POPs-contaminated sites (http://www.unido.org/index.php?id=1001169). The report can be downloaded from the internet.[14]

b) World Bank "*The Persistent Organic Pollutants (POPs) Toolkit*", which provides training modules and interactive tools for risk-based approaches to prioritize and manage POPs-contaminated sites and other hazardous substances (http://www.popstoolkit.com/).

A series of practical examples and best practice cases of PCDD/PCDF inventories for the most relevant source categories is included in the example inventory 11 including, where available, quantitative PCDD/PCDF data.

It is important to note that polluted sites, in particular at larger chemical production sites, are often impacted by a range of pollutants; contamination with PCDD/PCDF and other unintentional POPs may be coupled with pollution by other organohalogen compounds or heavy metals, which would also be included in the assessment of the site. For instance, chlor-alkali processes having used mercury technology have often resulted in a combination of mercury, PCDD/PCDF, PAH and other heavy metal contamination (Otto *et al*. 2006). All these aspects should be taken into account in the identification and inventory process of polluted sites.

The identification and inventory of polluted sites is merely a first step to manage related risks and for final cleanup and rehabilitation. A certain system of polluted sites management should thus be set up.

Polluted sites databases and registers

The inventory data should finally be integrated in a national database of contaminated sites. Taking into account the multi-pollutant nature of many contaminated sites, it is both practical and economic

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[14] http://www.unido.org/fileadmin/user_media/Services/Environmental_Management/Stockholm_Convention/POPs/toolkit/Contaminated%20site.pdf

to maintain a single national database for all contaminated sites, with information on the types of pollutants for the respective sites, including PCDD/PCDF, PCB and possibly other POPs.

Such national databases of contaminated sites have been developed over the last three decades in certain countries. For example, the United States Superfund program[15] is based on such a national inventory compilation of contaminated sites (see example inventory for source category 10l). Canada has a federal contaminated sites inventory which is publicly available, including PCDD/PCDF and PCB as listed pollutants.[16] Some countries have developed and published transparent guidelines to develop such inventories *e.g*. the Swedish EPA (Swedish EPA 2002).

Specific global or regional contaminated sites databases have also been established *e.g*. by the Blacksmith Institute (www.worstpolluted.org), Robin des Bois organization (www.robindesbois.org), the HCH and Pesticide Association (www.ihpa.info) (Vijgen *et al*. 2011).

The development of such inventories of contaminated sites can be framed by legislation requiring their establishment for the protection of future generation, and/or protection and management of soils and water resources. The European Commission has established such a requirement in the proposal of a soil framework directive (EC 2006).[17]

If a country already has a national database of contaminated sites, the information gathered via inventories of sites contaminated with PCDD/PCDF and other unintentional POPs will be added to the existing database. If such a database does not exist in a country, the establishment of a contaminated site inventory can initiate the development of a national contaminated sites inventory database.

Using the three phase approach the different categories and sites within the categories can be ranked and assessed according the priority setting based on risks. These assessments are also included in the contaminated sites inventory database.

10a Production Sites of Chlorine

Certain processes for the manufacture of chlorine have been associated with high formation and releases of PCDD/PCDF and other unintentional POPs (Weber *et al.* 2008). In addition to well-documented releases from the chlor-alkali process (Otto *et al.* 2006), earlier chlorine production using the Weldon or Deacon process has also resulted in PCDD/PCDF contaminated sites (Balzer *et al.* 2007, 2008).

I. Chlor-alkali production

The manufacture of chlorine using graphite anodes generates PCDD/PCDF contamination of the residues. Contamination levels close to 4 mg TEQ/kg in chlor-alkali residues have been reported; contaminated soil samples ranged from 0.15 µg I-TEQ/kg to 23.1 µg I-TEQ/kg (She and Hagenmaier 1994, Otto *et al.* 2006). The only chlor-alkali production site for which a PCDD/PCDF inventory has been published was operated in Rheinfelden/Germany. The deposited residues and contaminated soils were estimated to contain a total of 8.5 kg I-TEQ PCDD/PCDF from residues of the chlor-alkali process (see example 10aI).

Chlorine was produced almost exclusively using graphite anodes until it was gradually replaced by metal anodes and other technologies starting with the 1970s. The graphite residue was highly

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[15] http://www.epa.gov/superfund

[16] http://www.tbs-sct.gc.ca/fcsi-rscf/home-accueil-eng.aspx

[17] COM(2006)232, http://ec.europa.eu/environment/soil/three_en.htm

contaminated with PCDF, PCN and other chlorinated PAHs mainly from the reaction between chlorine and the pitch binder (Takasuga *et al.* 2009). In developing regions, graphite anodes have been used until recently and might possibly still be in use.

Primary locations for contamination from these operations include soil and, if leaching has occurred, neighbouring compartments and eventually sediments of nearby rivers. High concentrations of mercury could be an indicator for contamination with PCDD/PCDF as well. Barium levels in the deposited chlor-alkali residues were also found to be a useful and inexpensive monitoring parameter for tracking contamination of residues and deposits. This approach has been used for screening and mapping a German site impacted by widespread chlor-alkali residues (Otto *et al.* 2006; see example 10aI).

II. Leblanc process and associated chlorine/bleach production

High concentrations of PCDF (and minor concentrations of PCDD) were formed by Leblanc Soda and associated processes. PCDD/PCDF levels of up to 500 µg TEQ/kg have been reported in deposits from a former German Leblanc factory (Balzer *et al.* 2007, 2008; see example 10aII). The Leblanc process was extensively used until early 20th century to produce sal soda/sodium carbonate (Na_2CO_3) from sodium chloride (NaCl). The waste from this process (HCl) was recycled in some facilities by oxidation to produce chlorine/calcium hypochlorite (bleaching powder) either via manganese oxide (Weldon process) or by $CuCl_2$ catalysts (Deacon process) (Weber *et al.* 2008, Encyclopaedia Britannica 1911). The major source of PCDD/PCDF precursors was coal tar which was used as a filler and surface protection material. In addition to PCDD/PCDF, other unintentional POPs and chlorinated aromatic compounds were formed (Takasuga *et al.* 2009, Bogdal *et al.* 2008).

Leblanc factories were predominantly operated in the UK, France and Germany with a few facilities in other European countries (Balzer *et al.* 2008; see example 10aII). For inventories of former Leblanc factory sites, it is important to assess if the factory recycled HCl to chlorine/bleach, as recycling would be associated with high PCDD/PCDF levels in the wastes and likely contamination of the land where these wastes were deposited. In addition, PCDD/PCDF contamination has been found in areas where Leblanc ovens have been operated and since demolished (Balzer *et al.* 2008).

10b Production Sites of Chlorinated Organics

The largest PCDD/PCDF contaminated sites and hotspots have been generated by the production and application of chlorinated organics. For some production processes, other unintentional POPs were/are major residues. Furthermore, considerable quantities of product, either remaining in the residues or as faulty batches, were deposited on or close to the production sites. A prime example is lindane/HCHs, with only approximately 15% of the total mass emerging as product, and the remaining 85% representing HCH waste isomers, dumped in the vicinity of the production facilities. The production of DDT and endosulfan also generate large amounts of wastes containing POPs which have often been landfilled. Wastes from the organochlorine industry are now destroyed in BAT/BEP incinerators in developed regions. However, these wastes were often landfilled or dumped until the 1970s/1980s. In developing regions, such wastes might still be landfilled nowadays.

The inventory of such production sites and related contaminated sites should consider:

- The former and current production portfolio should be assessed for chemicals containing or possibly containing PCDD/PCDF, HCB or other unintentional POPs (see Annex 2 and example 10bIII). The highest concentrations of PCDD/PCDF are expected to be associated with the production of chlorinated phenols, their derivatives, and other chlorinated aromatic compounds. However the production of non-aromatic chemicals like chlorinated solvents has also generated wastes containing unintentional POPs *e.g*. 10,000 tons of unintentionally produced HCB from single production sites (Weber *et al.* 2011).

- Former and current management practices for waste residues should be reviewed and an inventory of related production sites, stockpiles and landfills should be developed (see examples 10bII and 10bIII).
- Contamination with PCDD/PCDF of buildings and soil is likely to be found at current or former production sites of chlorinated organics.
- If wastewater was discharged into receiving waters, sediments and floodplains of entire river systems or bays can be contaminated (see example 10bI).
- If wastewater has been allowed to settle in ponds, sediment or sludge from these settling ponds can contain high concentrations of PCDD/PCDF.

I. Production sites of chlorophenol

High concentrations of PCDD/PCDF can be expected at sites where chlorinated phenols were produced. In the case of Times Beach, USA, where production residues were spread, contaminated soils have been reported as having concentrations of up to 33,000,000 ng TEQ/kg (Rappe 1984). Levels around factories can be as high as 200,000 ng TEQ/kg (di Domenico *et al.* 1982). Where production residues have been released via water discharge, sediments can be polluted with tens of kg TEQ (Verta *et al.* 2008; see example 10bI). PCDD/PCDF in related deposits are reported to total 7.7 kg TEQ for a PCP production facility in Germany (Otto *et al.* 2006; see example 10bI) and 22.3 kg from a 2,4,5-T production site also located in Germany (Götz *et al.* 2012).

II. Former lindane production where HCH waste isomers have been recycled

In the production of lindane (gamma-HCH), approximately 85% HCH waste isomers are formed in the chlorination step of benzene as unintentional POPs (Vijgen *et al.* 2011). The active gamma-isomer used to be separated and the remaining 85 to 90% waste isomers, consisting mainly of alpha-HCH and some beta, delta and epsilon-HCH, were dumped. This practice has generated the largest international POPs stockpile, estimated at 4 to 7 million tons, often dumped in the vicinity of the factories (Vijgen 2006a,b, Vijgen *et al.* 2011). To avoid such dumping, waste isomers have been recycled at some production sites (Vijgen *et al.* 2011; see example 10bII). Recycling of HCH by thermal decomposition to produce technical tri/tetrachlorbenzene generated highly contaminated residues containing 1.4 to 13% PCDD/PCDF with I-TEQ in the high ppm range (90 to 610 ppm) (Vijgen *et al*. 2011, Zheng *et al.* 1999). The total PCDD/PCDF amount in registered waste disposed of by a German factory was estimated to be between 333 and 854 kg PCDD/PCDF I-TEQ (53 -102 tons total PCDD/PCDF) (Götz *et al.* 2012; see example 10bII). Since the recycling of HCH waste has been carried out at several lindane production sites, related contamination can also be expected at these sites (Vijgen *et al.* 2011).

III. (Former) production sites of other chemicals known or suspected to contain PCDD/PCDF or other unintentional POPs

A wide range of production residues from organochlorine chemicals can be considered to be contaminated with PCDD/PCDF or other unintentional POPs (see Annex 2). Some data may be available for levels in products (see Source Group 7), however data on levels of PCDD/PCDF or other unintentional POPs in the residues have not been published. Emission factors for most residues are currently not available and will depend on the specific technologies used. Detailed data for the inventory need to be generated for the individual sites including information on the (former) products and intermediates and the respective management and disposal procedures. These production sites and related deposits can be inventoried as potentially contaminated with PCDD/PCDF, noting that "further assessment is necessary". As an example, an inventory has been compiled for the production wastes generated and landfilled by the Basel Chemical Industry (see example 10bIII).

IV. Production sites of chlorinated solvents and other "HCB waste"

In the production of certain solvents (*e.g.* carbon tetrachloride, tetrachloroethene, trichlorobenzenes, trichloroethene, trichlorotoluenes), large amount of wastes containing HCB as a prime contaminant ("HCB waste") are generated (Jacoff *et al.* 1986, Jones *et al.* 2005). For one facility, an emission factor of 1.8% was calculated on the basis of the solvents produced (see example 10bIV; Weber *et al.* 2011b). Other studies have estimated that 4% of "HCB waste" is generated from tetrachloroethene production. For some solvent production, it is reported that individual factories have deposited or stored some 10,000 tons HCB waste (Weber *et al.* 2011a,b). Some of these wastes also contained relevant levels of PeCB (see example 10bIV).

For an inventory of deposits and dumps from solvent production, the following steps are recommended:

- Establish the total quantities of organochlorine solvent produced at the site.
- Establish whether specific factors for factory-generated wastes or data on the total deposited wastes are available. Otherwise a factor of 2% "HCB waste" for the solvents mentioned above can be used.
- Assess the waste management practices over time *i.e*. the time over which the wastes have been deposited, when improved treatment/destruction capacity for production residues was added.
- Map and assess the deposits, associated contamination and related risks.

HCB is also the prime unintentional POP contaminant in the production of certain pesticides (*e.g.* PCNB, PCP, dacthal, daconil, hexachlorcyclopentadiene) (Jacoff *et al.* 1986) and of tetrachlorophthalic acid and related dyes such as chlorinated phthalocyanines (Government of Japan 2007). A similar approach to the assessment of "HCB waste" from solvents can be used for these sites.

V. (Former) PCB and PCB-containing materials/equipment production

PCB and PCB-containing materials (varnish/paints, sealants, etc.) were produced at chemical plants, and PCB-containing equipment at electrotechnical plants. According to Fedorov (2003) and Ishankulov (2008), annual releases of PCB into the environment from production processes of PCB-containing capacitors at the Ust-Kamenogorsk plant in Kazakhstan generated some 188-227 tons PCB (10-12% of the total PCB used). These releases lead to significant environmental contamination with PCB and PCDD/PCDF, in particular at production sites. These sites can thus be treated as potential hotspots. In addition, storage sites of solid waste and sewage sludge from such facilities are also potential hotspots.

The procedure for revealing such hotspots includes the steps described below:

- A compilation of a list of enterprises where PCB and PCB-containing materials/equipment have been produced;
- Collection of general information about the enterprises (location, the area occupied by the plant, production timeframe, volume of PCB production or PCB used, volume of PCB-containing waste, waste water and sewage sludge, emissions via these vectors, etc);
- Localization of dumps of PCB-containing waste and sewage sludge storage;
- Collect information on PCB leakages, monitoring of POPs content in the environment, etc;
- Estimation of PCDD/PCDF discharges into the environment based on PCB leakages data.

10c Application Sites of PCDD/PCDF Containing Pesticides and Chemicals

These sites include locations where pesticides and other chemicals containing PCDD/PCDF have been applied. Dioxin-containing herbicides/pesticides such as 2,4,5-T, 2,4-D, PCP or others have been applied in agriculture or for clearing vegetation. In Vietnam, spraying of the defoliant Agent Orange and other 2,4,5-T/2,4-D containing agents during 1963-1970 caused extensive environmental contamination and human exposure (Schecter 1994, Allen 2004) releasing some 366 kg TEQ (Stellmann *et al.* 2003). A comprehensive inventory for historic agricultural pesticide use (mainly PCP and CNP) has been established for Japan and is estimated at 460 kg TEQ, having migrated partly from agricultural fields to river sediments and sea (see example 10c). The human milk contamination measured in Japan today is correlated to former pesticide use (Tawara *et al.* 2006, Weber *et al.* 2008).

The use of other organochlorine chemicals having resulted in large contaminated sites are *e.g.* solvents such as tetrachloethene or trichlorethene, which can be contaminated with HCB and PeCB.

For establishing a country inventory, either own PCDD/PCDF data measured from historic pesticides and other chemicals, or emission factors established by other studies might be used (see example 10c). The impacted areas and nearby river systems should be included in the inventory. PCDD/PCDF levels in grazing animals and milk, or in fish in the affected water systems might be assessed.

10d Timber Manufacture and Treatment Sites

Saw mills and timber manufacturing sites are often associated with the use of pentachlorophenol. Soils and sediments can be contaminated with PCDD/PCDF as these industries use large volumes of water and are often located close to rivers. The application of PCP in Sweden, for example, has released between 5 and 50 kg TEQ on these sites, and a further 200 kg TEQ in the product (Swedish Environmental Protection Agency 2005). As PCP and PCP-Na have a much higher water solubility and shorter half-lives, the concentration of PCP in soils or sediments can only give approximate indications of PCDD/PCDF contamination.

Inventories can be established using former application quantities and contamination levels. In addition to an inventory of PCP application sites, a rough inventory of former PCP use and related PCDD/PCDF in treated wood might be established.

10e Textile and Leather Factories

PCDD/PCDF and other unintentional POPs containing chemicals like PCP, chloranil and certain dyes have been, and sometimes still are, used in this sector. Contaminated sites or hotspots can be expected at production sites where these chemicals have been stored, used and discharged. In particular, adjacent sediments and waste deposits are likely to be contaminated. Areas where sludges from production or from wastewater treatment have been applied can also be contaminated and should be included in the inventory.

10f Use of PCB

The use of PCB has generated a large number of sites and hotspots contaminated with PCDF and dioxin-like PCB via production, use in industries, releases from equipment and open applications (see examples 10fI and 10fII). Commercial mixtures of PCB contain dioxin-like PCB, non-dioxin-like PCB and PCDF, with a major TEQ contribution (> 90%) from dioxin-like PCB (Takasuga *et al.* 2005). PCDF releases can only be estimated based on of the amount of PCB leaked. For this assessment, the total TEQ of PCDF and dioxin-like PCB needs to be considered. With the increasing age of the equipment and longer time of operation, PCDF concentrations in equipment fillings increase, and in the case of high thermal stress (fire event, short circuit) PCDF become the main TEQ contributor.

About 60% of the total volume of PCB was used as dielectric fluids in transformers and power capacitors globally (Breivik *et al.* 2007, Willis 2000). The open uses of PCB, largely as sealants and paints in buildings and in industrial installations, can be considered as hotspots.

If the transformers and capacitors are in a good condition and well maintained, with no leakage, PCB and PCDF are not released into the environment. Once the equipment is leaking, PCDF together with PCB and possibly PeCB will subsequently be released into the surroundings, in soils and sediments. PCB can serve as an indicator for PCDF contamination.

Sites with PCB-containing equipment in use or storage should be treated as potential hotspots. The number of such sites per country may be rather large (see example 10fI; Kukharchyk and Kakareka 2008).

The main tasks for inventorying PCB-contaminated sites and hotspots are:

- Identification/localization of sites where PCB-containing transformers and capacitors are in use or stored, including damaged equipment and PCB waste and sites of open PCB application;
- Identification of PCB leakage;
- Development of the hotspot list;
- Assessment of volumes of PCB leakage and releases of PCDD/PCDF.
- Assessment of PCDD/PCDF concentrations in
    - PCB transformers/capacitors from producers where PCDF levels are currently unknown;
    - Sites where transformer fires, short circuits or other fires involving PCB have occurred.

The identification and assessment can be performed based on a tiered approach as presented below.

1. Baseline approach

The basis for hotspots accounting is the national inventory of PCB according to Annex A, Part II of the Stockholm Convention. All sites where PCB-containing equipment can be found in use or storage are treated as hotspots. The baseline approach allows the assessment of the total number of potential hotspots, total volumes of PCB and PCDD/PCDF in PCB-containing equipment, as well as potential leakages of PCB and PCDD/PCDF into the environment, using the results of the national PCB inventory.

To differentiate between lower and higher chlorinated PCB congeners, as needed for estimating PCDD/PCDF releases, it can generally be assumed that capacitors are filled with lower chlorinated PCB, while transformers include higher chlorinated PCB with associated PCDD/PCDF levels (Table II.10.1).

For a preliminary assessment of PCB releases into the environment, emission factors given in the EMEP/EEA Atmospheric Emission Inventory Guidebook (2009) may be used (Table II.10.1). Using data on the volumes of lower and higher chlorinated PCB and PCDD/PCDF content in PCB liquids (Table II.10.2), it is possible to estimate PCDD/PCDF and dioxin-like PCB content in PCB equipment and their environmental releases.

Table II.10.1 PCB release factors from electrical equipment

10f	PCB Filled Transformers and Capacitors	PCB release (kg/t dielectric fluid)	Country or region
1	Transformers	0.06	Europe
		0.3	North America
		0.3	CIS countries
2	Capacitors	1.6	Europe
		4.2	North America
		2.0	CIS countries

Table II.10.2 Concentrations of PCDD/PCDF and dioxin-like PCB in unused commercial PCB

PCB type	PCDD/PCDF in unused commercial PCB (µg TEQ/t product)	Dioxin-like PCB (µg TEQ/t product)*
Low chlorinated, *e.g.*, Clophen A30, Aroclor 1242	7,000 – 15,000	1,900,000-3,500,000
Medium chlorinated, *e.g.*, Clophen A40, Aroclor 1248; KC-400; KC-500	23,000 – 70,000	12,000,000-16,000,000
Medium chlorinated, *e.g.*, Clophen A50, Aroclor 1254	300,000	12,000,000-16,000,000
KC-600; KC-1000	22,000	4,100,000 - 10,000,000
High chlorinated, *e.g.*, Clophen A60, Aroclor 1260	1,500,000	4,100,000 - 10,000,000

*Data for dioxin-like TEQ in low, medium and high chlorinated PCB are derived from PCB mixtures (Takasuga *et al.* 2005).

If the results of the PCB inventory contain detailed PCB data per site and a clear indication of sites, the list of potential hotspots should be compiled. It should contain the details of the location, coordinates, facility name, type and number of PCB-containing equipment, volume of PCB and the state of the equipment. This list can then serve as a basis for further investigation of hotspots.

2. Detailed approach

The detailed approach is used when the results of the national PCB inventory are partial, inaccurate or not applicable for the identification of hotspots. In such cases, additional questionnaires are sent to governmental bodies, state offices or directly to facilities which hold or operate PCB-containing equipment. In addition to usual questions on the number of PCB-filled equipment, the questionnaires should also enquire on PCB leaks, accidents involving such equipment, description of sites with PCB, results of analysis of PCB in soils and water etc.

3. Comprehensive approach

Through the comprehensive approach, in addition to the results of the national PCB inventory and/or questionnaires to owners of PCB-filled equipment, special investigations of PCB-filled equipment or storage sites are organised, including on-site inspection, soil and other media sampling and analysis, estimation of polluted areas, volumes of leakages, PCB stocks in soil, depth of pollution, risk assessment etc. During the first stages, priority should be given to sites with the largest stocks of PCB-filled equipment, sites with accidents and significant leakages and sites with the highest risk of water and soil pollution.

The results of such a comprehensive inventory allow the preparation of a detailed register of hotspots, with the indication of their prioritisation for remediation measures.

As for the presentation of results of the hotspot inventory (applying the baseline and detailed approach), these can be included in the relevant Excel file (in Source Group 10); the number of identified hotspots, volumes of PCB in equipment (and distribution between lower and higher chlorinated congeners) are needed as input to estimate PCDD/PCDF releases from these sources. For the comprehensive inventory, separate reports are prepared.

10g Use of Chlorine for Production of Metals and Inorganic Chemicals

In addition to organochlorine industry, chlorine was/is used in a range of other industries, resulting in PCDD/PCDF containing residues and releases. For example, pulp and paper sludge from bleach process using elemental chlorine have been highly contaminated with PCDD/PCDF and other chlorinated compounds. The application of such sludges to land or through dumping of sludges resulted in hotspots or contaminated land (see example 10g).

Elemental chlorine either remains in the final product (*e.g*. HCl, NaOCl, ClO_2, phosphorous chlorides or metal chlorides) or is simply used in the process (*e.g*. titanium dioxide, magnesium or silicon) (Stringer and Johnston 2001). For some of these processes, high PCDD/PCDF formation and release potential has been documented. Contaminated sites have been assessed worldwide, *e.g.* magnesium production in Norway which polluted several fjords and associated food webs with an estimated total PCDD/PCDF release between 50 and 100 kg TEQ (Knutzen and Oehme 1989). The production of titanium dioxide using chlorine process can also generate PCDD/PCDF in the order of kg/year (Wenborn *et al*. 1999).

For an inventory of contaminated sites from processes using chlorine *e.g*. production of pulp and paper, magnesium production, TiO_2, former releases of these productions, impacted sediments and deposits of residues should be considered.

10h Waste Incinerators

Emissions from non-BAT incinerators can result in the contamination of milk, eggs or vegetables in the surroundings of incinerators (Liem *et al.* 1991, Schmid *et al*. 2003, DiGangi and Petrlík 2005, Watson 2001). In particular, non-BAT incinerators that process organochlorine products, especially PCDD/PCDF precursors (PCB, chlorophenols, chlorobenzenes and other chlorinated aromatics), can result in high emissions of PCDD/PCDFs with considerable impacts on the local environment (Holmes *et al*. 1994, 1998). Only a limited number of cases of PCDD/PCDF contaminated sites from waste incinerators have been documented to date, showing that release vectors from incinerators - air, solids and water - can lead to PCDD/PCDF contaminated sites if not appropriately managed and controlled (see example 10h). The areas around incinerators can also be contaminated from spills of hazardous chemicals treated/destroyed in these facilities.

For the inventory of PCDD/PCDF contaminated sites from incinerators (and other thermal facilities), (former) management practices and disposal of ashes (in particular fly ash and APC residues) and water release from wet scrubbers[18] should be assessed. Contaminated sites via deposition from air releases are only expected for non-BAT incinerators which emit high PCDD/PCDF levels over extended time periods. In addition to soil measurements, PCDD/PCDF levels in eggs or cow's milk in the vicinity of the incinerator are potentially good indicators of the contamination status.

10i Metal Industries

A limited number of PCDD/PCDF contaminated sites associated with metal industries have been documented. Typically, toxic heavy metals represent the key contaminants for sites associated with these industries, while PCDD/PCDF are generally regarded as minor by-products.

Releases from primary metal production processes can cause PCDD/PCDF contaminated sites via distribution of metal industry slag, as recorded in Germany. In this case, more than 400,000 tons of slag from a specific primary copper production process, which was highly contaminated with PCDD/PCDF (10,000 to 100,000 ng TEQ/kg), was used as a surface cover for more than 1,000 sports fields, playgrounds and pavements in Germany and neighbouring countries (Ballschmiter and Bacher 1996, Theisen *et al.* 1993). PCDD/PCDF contaminated sites around a sinter plant in Italy have also resulted in restrictions on grazing (Diletti *et al*. 2009). Emissions from a secondary copper smelter in Rastatt/Germany contaminated surrounding soils, including residential areas, with PCDD/PCDF levels above the German limit values for contaminated soils (Hagenmaier *et al.* 1992).

For the inventory of PCDD/PCDF (and heavy metal) hotspots and contaminated sites, the air releases over years/decades should be considered as well as the management and disposal of ashes.

10j Fire Accidents

Fires can produce soot and residues with elevated concentrations of PCDD/PCDF (see also category 6b). High levels of contamination result from fires where chlorinated aromatic compounds are burned such as PCB transformer fires or fires of pesticide stocks or other organochlorine stockpiles.

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[18] According to BAT, wet scrubbers operate in closed cycles with phase out of the salt and appropriate deposition.

Fires in buildings with concentrated amounts of flame retarded material or high level of PVC can also result in high PCDD/PCDF releases and deposition, normally concentrated in the soot (see example 10j). The soot should thus be collected and disposed of properly as hazardous waste.

10k Dredging of Sediments and Contaminated Flood Plains

Sediments from harbours or downstream of industrial discharge pipelines from any of the above-listed industrial activities can be contaminated with PCDD/PCDF, HCB and other pollutants like heavy metals. Very often, to maintain access through channels, these sediments are dredged and deposited on land. This activity only removes PCDD/PCDF contamination from its location and from the aquatic environment, and transfers the same level of contamination to another location with potentially new exposures. When inventories of dredging activities are established, the deposition of sediments on areas used for agriculture and residential housing should be highlighted and possibly assessed for levels of contamination.

Rivers with a history of PCDD/PCDF contamination can have PCDD/PCDF contaminated floodplains in addition to polluted sediments. Since floodplains are often used for grazing or in agriculture, the inventory and management of impacted floodplains should be performed to prevent human exposure (see example 10k).

10l Dumps of Wastes/Residues from Source Groups 1-9

Where PCDD/PCDF containing products or residues have been disposed of, there is a probability that these contaminants will be released into the environment. PCDD/PCDF are relatively immobile in dumps or landfills as long as there are no organic co-deposits facilitating leaching or seepage water capable of mobilizing the contamination. Of particular importance is the remobilization of PCDD/PCDF-containing deposits if such landfills or dumps are excavated due to remediation measures or for mining purposes (see category 9a; see example 10l).

Chemical or otherwise hazardous landfills containing PCDD/PCDF are sometimes secured by engineering measures. Because of their persistence, PCDD/PCDF and other unintentional POPs will persist in landfills for many decades or centuries (Balzer *et al*. 2008). Over these extended time frames, engineered landfill systems, including liners, gas and leachate collection systems will inevitably degrade and lose their structural integrity and capability to contain persistent contaminants (Allen 2001, Weber *et al*. 2011a).

Landfills and deposits should thus be inventoried and included in a database. In a systematic inventory of landfills/dumps within a country, the specific presence of PCDD/PCDF and other unintentional POPs should be included.

10m Kaolin or Ball Clay Sites

Ball clay and kaolinic clays in different regions in the world can contain PCDD/PCDF with a specific OCDD dominated pattern (Ferrario *et al.* 2007, Horii *et al*. 2011). A first global inventory has been established by Horii *et al*. (2011). Typical for all samples is the almost total absence of PCDF, and the nearly identical congener/isomer distribution throughout all geographies. Thus, PCDD appear to have been formed by natural processes possibly millions of years ago (Ferrario *et al*. 2007, Horii *et al*. 2011). Kaolin samples from Africa have also been found to contain elevated levels of PCDD (Hogenboom *et al.* 2011). Studies also show that the relative high levels of PCDD/PCDF in human milk samples from Congo and Ivory Coast are due to the use of the clay during pregnancy (see example

10m). PCDD/PCDF in ball/kaolinic clays, in particular from quarries where clays are used for human consumption or as animal feed additive, should thus be included in the inventory.