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Matters related to the implementation of the Convention: scientific and technical matters: technical guidelines

# **Technical guidelines**

Technical guidelines on the environmentally sound management of wastes containing or contaminated with unintentionally produced polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, hexachlorobenzene, polychlorinated biphenyls or pentachlorobenzene

#### Note by the Secretariat

At its twelfth meeting, the Conference of the Parties to the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal adopted, in decision BC-12/3 on technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with persistent organic pollutants, the technical guidelines on the environmentally sound management of wastes containing or contaminated with unintentionally produced polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, hexachlorobenzene, polychlorinated biphenyls or pentachlorobenzene, on the basis of the draft technical guidelines contained in document UNEP/CHW.12/5/Add.4. The technical guidelines referred to above were prepared by the Chemicals Branch of the Division of Technology, Industry and Economics of the United Nations Environment Programme (UNEP Chemicals) as lead organization for this work, in close consultation with the small intersessional working group on the development of technical guidelines on persistent organic pollutants wastes and taking into account comments received from parties and others and comments provided at the ninth meeting of the Open-ended Working Group of the Basel Convention. The technical guidelines were further revised on 10 April 2015 taking into account comments received from parties and others by 23 January 2015, as well as the outcome of the face-to-face meeting of the small intersessional working group on the development of technical guidelines on persistent organic pollutants wastes held from 17 to 19 March 2015 in Ottawa, Canada (see document UNEP/CHW.12/INF/11). The text of the final version of the technical guidelines, as adopted, is set out in the annex to the present note.

#### Annex

Technical guidelines on the environmentally sound management of wastes containing or contaminated with unintentionally produced polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, hexachlorobenzene, polychlorinated biphenyls or pentachlorobenzene

**Revised final version (15 May 2015)** 

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# Abbreviations and acronyms

	-
2,4,5-T	2,4,5-trichlorophenoxyacetic acid
2,4-D	2,4-dichlorophenoxyacetic acid
BAT	best available techniques
BEP	best environmental practices
CCMS	Committee on the Challenges of Modern Society
CEN	European Committee for Standardization
DDT	1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (dichlorodiphenyltrichloroethane)
ESM	environmentally sound management
HCB	hexachlorobenzene
HRGC	high resolution gas chromatorgaphy
HRMS	high resolution mass spectrometry/spectrometer
I-TEFs	international toxicity equivalency factors
ISO	International Organization for Standardization
NATO	North Atlantic Treaty Organisation
OJEU	Official Journal of the European Union
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzo-p-dioxin
PCDF	polychlorinated dibenzofura
PCNB	pentachloronitrobenzene
PeCB	pentachlorobenzene
PER, PERC	perchloroethylene
POP	persistent organic pollutant
TCDD	2,3,7,8-tetrachlorodibenzo-p-dioxin
TEFs	toxicity equivalency factors
TEQ	toxic equivalenty
UV	ultraviolet
WHO	World Health Organization
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# Units of measurement

μg	microgram
mg	milligram
µg/kg	microgram per kilogram
mg/kg	milligram per kilogram
ppb	parts per billion
ppm	parts per million

# I. Introduction

#### A. Scope

1. The present technical guidelines provide guidance on the environmentally sound management (ESM) of wastes containing or contaminated with unintentionally produced polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), hexachlorobenzene (HCB), polychlorinated biphenyls (PCB) or pentachlorobenzene (PeCB), pursuant to several decisions of two multilateral environmental agreements on chemicals and wastes.<sup>1</sup> PCDD, PCDF, HCB and PCB were listed in Annex C to the Stockholm Convention at the time of the adoption of the Convention. PeCB was listed in Annex C to the Convention in 2009 and the amendment entered into force in 2010.

2. This document supersedes the *Technical guidelines on the environmentally sound management* of wastes, containing or contaminated with unintentionally produced polychlorinated dibenzo-pdioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), hexachlorobenzene (HCB) or polychlorinated biphenyls (PCBs) of March 2007.

3. The present technical guidelines cover all the persistent organic pollutants (POPs) that are formed and released unintentionally from anthropogenic sources as listed in Annex C of the Stockholm Convention ("Unintentional Production"), i.e. HCB, PeCB, PCDD and PCDF.

4. Intentionally produced POPs are not covered by the present technical guidelines but are the subject of the following specific technical guidelines:

(a) Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with polychlorinated biphenyls (PCBs), polychlorinated terphenyls (PCTs) or polybrominated biphenyls (PBBs) including hexabromobiphenyl (HBB) (UNEP, 2015);

(b) Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with the pesticides aldrin, alpha hexachlorocyclohexane, beta hexachlorocyclohexane, chlordane, chlordecone, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), lindane, mirex, pentachlorobenzene, perfluorooctane sulfonic acid, technical endosulfan and its related isomers or toxaphene or with HCB as an industrial chemical (Pesticide POPs technical guidelines) (UNEP, 2015a);

(c) Technical guidelines for the environmentally sound management of wastes consisting of, containing or contaminated with 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (DDT) (UNEP, 2006);

(d) Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF) (UNEP, 2015b);

(e) Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with hexabromodiphenyl ether (hexaBDE) and heptabromodiphenyl ether (heptaBDE) or tetrabromodiphenyl ether (tetraBDE) and pentabromodiphenyl ether (pentaBDE) (UNEP, 2015c);

(f) Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with hexabromocyclododecane (UNEP, 2015d).

5. The present document should be used in conjunction with the *General technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with persistent organic pollutants* (hereinafter referred to as "general technical guidelines") (UNEP, 2015e). The general technical guidelines are intended to serve as an umbrella guide for the ESM of wastes consisting of, containing or contaminated with POPs, and provide more detailed information on the nature and incidence of wastes containing or contaminated with unintentionally produced POPs for purposes of their identification and management.

<sup>&</sup>lt;sup>1</sup> Decisions IV/17, V/26, VI/23, VII/13, VIII/16, BC-10/9, BC-11/3 and BC-12/3 of the Conference of the Parties to the Basel Convention on the Control of Transboundary Movement of Hazardous Wastes and Their Disposal; decisions OEWG-I/4, OEWG-II/10, OEWG-III/8, OEWG-IV/11, OEWG-V/12, OEWG-8/5 and OEWG-9/3 of the Open-ended Working Group of the Basel Convention; Resolution 5 of the Conference of Plenipotentiaries to the Stockholm Convention on Persistent Organic Pollutants; decisions INC-6/5 and INC-7/6 of the Intergovernmental Negotiating Committee for an International Legally Binding Instrument for Implementing International Action on Certain Persistent Organic Pollutants; and decisions SC-1/21, SC-2/6, SC-4/16, SC-5/9 and SC-6/11 of the Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants.

6. In the present document, reference is made to the PCBs technical guidelines and the Pesticide POPs technical guidelines when the information is common to both unintentionally and intentionally produced POPs.

#### B. Description, production and wastes

#### 1. Description

#### (a) PCDD and PCDF

7. PCDD and PCDF are tricyclic halogenated aromatic hydrocarbons consisting of two benzene rings connected by two oxygen atoms at adjacent carbons on each of the benzene rings in PCDD and by one oxygen atom and one carbon-carbon bond at adjacent carbons in PCDF. The basic structures of unchlorinated compounds are shown in figure 1 below.

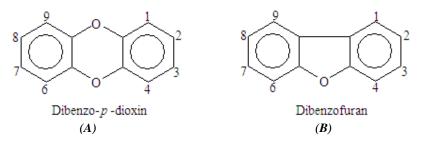


Figure 1: Structures of dibenzo-para-dioxin (A) and dibenzofuran (B)

8. Both groups of chemicals may have up to eight chlorine atoms attached at carbon atoms 1 to 4 and 6 to 9. Each of the compounds resulting from chlorine substitution is referred to as a congener. The number and position of chlorine atoms around the aromatic nuclei distinguish each specific congener. In total, there are 75 possible PCDD congeners and 135 possible PCDF congeners. The most widely studied of the PCDD and PCDF is 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD).

9. Congeners with up to three chlorine atoms are thought to be of little toxicological significance. However, 17 congeners with chlorine atoms in the 2, 3, 7 and 8 positions (i.e., in the lateral positions of the aromatic rings) have shown to pose a health and environmental risk. Increasing substitution from four to eight chlorine atoms generally results in a marked decrease in potency.

10. PCDD and PCDF have very low water solubility, high octanol-water partition coefficients, low vapour pressures strong adsorptivity to particles and surfaces and are resistant to chemical and biochemical degradation under environmental conditions. Consequently, they persist in the environment and their high fat solubility and inherent stability results in their bioconcentration and accumulation in the food chain. Almost all 210 PCDD and PCDF congeners have been identified in emissions from thermal and industrial processes and as a result they are found as mixtures in environmental matrices such as soil, sediment, air, plants and lower animals, although their low aqueous solubility means that they can hardly be detected in water. Due to their chemical-physical properties, PCDD/PCDF are largely immobile in soils.

11. When found in the environment, biological tissues and industrial sources, PCDD and PCDF are usually present as complex mixtures and their various congeners vary significantly in their concentrations. The potency of PCDD and PCDF has been ranked relative to 2,3,7,8-TCDD, the most toxic member of the dioxin class. Those rankings are known as toxicity equivalency factors (TEFs). To be included in the TEF scheme, a PCDD or PCDF must bind to the cellular aryl hydrocarbon (Ah) receptor, elicit Ah receptor-mediated biochemical and toxic responses, be persistent, and accumulate in the food chain (WHO, 1998; van den Berg et al., 1998 and 2006). To estimate the toxic potency of a given mixture of PCDD and PCDF, the mass concentration of each congener is multiplied by its TEF and the products are summed to give the toxicity equivalence (TEQ) of the mixture.

12. The most recent review of TEFs was that carried out by an expert group for the World Health Organization in 2005 (van den Berg et al., 2005). Under the WHO TEF scheme, TCDD is assigned a TEF of 1.0 and other PCDD and PCDF have TEF values ranging from 1.0 down to 0.0001. The WHO TEF scheme also includes those PCB congeners which are considered to exhibit dioxin-like characteristics; their TEFs range from 0.1 down to 0.00001. The WHO TEF scheme has established three separate schemes, one for humans and other mammals and two others for birds and fish, respectively. For human risk assessment, the human/mammalian TEFs should of course be applied.

13. It should be noted that much national legislation still applies the earlier international TEF (I-TEF) scheme, which was established by the North Atlantic Treaty Organisation Committee on the Challenges of Modern Society (NATO/CCMS) in 1988. That I-TEF scheme includes only the 17 PCDD and PCDF congeners with chlorine atoms substituted in the 2, 3, 7 and 8 positions and does not include dioxin-like PCB.

14. Under Annex C to the Stockholm Convention, concentrations should be reported commencing with the 1998 WHO TEF scheme. It is noteworthy that this is not the most recent evaluation coordinated by WHO.

#### (b) PCB

15. For information, see subsection I.B.1 (a) of the PCBs technical guidelines.

#### (c) HCB

16. For information, see subsection I.B.7 (a) of the Pesticide POPs technical guidelines.

#### (d) PeCB

17. For information, see subsection I.B.10 (a) of the Pesticide POPs technical guidelines.

#### 2. Unintentional production

18. Under Article 5 of the Stockholm Convention, parties are required to reduce total releases from anthropogenic sources of the chemicals listed in Annex C (i.e., unintentionally produced PCDD, PCDF, HCB, PCB and PeCB) with the goal of their continuing minimization and, where feasible, ultimate elimination.

#### (a) PCDD and PCDF

19. PCDD and PCDF have never been intentionally produced or used commercially except in very small quantities for analytical and research purposes.

20. PCDD and PCDF are unintentionally formed in **industrial-chemical processes**, such as chemical manufacture, and **thermal processes**, such as waste incineration when carbon, oxygen, hydrogen and chlorine, whether in elemental, organic or inorganic form, are present. At some point in the synthesis process, whether present in a precursor or generated by a chemical reaction, the carbon atoms must assume an aromatic structure.

21. PCDD and PCDF may occur as trace contaminants in a number of chemical products when carbon, hydrogen, oxygen and chlorine are present. It is thought that one or more of the following conditions favour PCDD/PCDF formation in chemical processes (UNEP, 2006; UNEP, 2013a):

- (a) Elevated temperatures (> 150°C);
- (b) Alkaline conditions;
- (c) Metal catalysts;
- (d) Ultraviolet (UV) radiation or other radical starters.

22. Chemical processes that may lead to the formation of PCDD/PCDF include the manufacture of chlorophenols, such as pentachlorophenol. The propensity for PCDD/PCDF formation in the manufacture of chlorophenols has been reported as follows:

Chlorophenols > chlorobenzenes > chlorinated aliphatics > chlorinated inorganics.

23. PCDD/PCDF may also be formed as unintentional by-products in combustion processes, mainly at temperatures between 200°C and 650°C, with a peak around 300°C. Consequently, they may be formed as unintentional products in certain processes in which carbonaceous material is heated in the presence of organic or inorganic chlorinated substances (including sodium chloride, i.e., common salt) together with oxygen or oxygen-containing compounds under certain conditions of temperature, residence time, humidity and catalyst presence.

24. In thermal processes, there are two main pathways by which PCDD/PCDF can be synthesized: from precursors, such as chlorinated phenols, or *de novo* from carbonaceous structures in fly ash, activated carbon, soot or smaller molecule products of incomplete combustion. Under conditions of poor combustion, PCDD/PCDF can be formed in the burning process itself.

25. Among the variables and conditions that affect the formation of PCDD/PCDF in thermal processes, the following play an important role (UNEP, 2006):

(a) Technology: PCDD/PCDF formation can occur either as a result of poor combustion techniques or poorly managed post-combustion chambers and air pollution control devices. Combustion techniques vary from the very simple and very poor, such as open burning, to the very complex and greatly improved, such as incineration using best available techniques;

(b) Temperature: PCDD/PCDF formation in the post-combustion zone or air pollution control devices has been reported to range between 200°C and 650°C; the range of greatest formation is generally agreed to be 200–450°C, with a maximum of about 300°C;

(c) Metals: Copper, iron, zinc, aluminium, chromium and manganese are known to catalyse PCDD/PCDF formation, chlorination and dechlorination;

(d) Sulphur and nitrogen: Sulphur and some nitrogen-containing chemicals inhibit the formation of PCDD/PCDF, but may give rise to other unintended products;

(e) Chlorine: chlorine must be present in organic, inorganic or elemental form. Its presence in fly ash or in the elemental form in the gas phase may be especially important;

(f) PCB: PCB are also precursors to the formation of PCDF.

26. A comprehensive list of sources that may release PCDD and PCDF and, to a lesser extent, other unintentional POPs listed to Annex C to the Stockholm Convention into the environment is presented in the *Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional Persistent Organic Pollutants under Article 5 of the Stockholm Convention* (UNEP, 2013a) (hereinafter referred to as "Toolkit for unintentional POPs"), which contains guidance for developing release inventories of unintentionally produced POPs.

#### (b) PCB

27. PCB may be formed and released from the same sources that generate and release PCDD/PCDF (UNEP, 2006); these sources include the inappropriate operation of incinerators and the combustion of waste at inadequate temperatures, especially during open-air and other open burning of wastes. Furthermore, recently PCB have been identified as unwanted contaminants in a number of dye pigments (Grossman, 2013).

#### (c) HCB

28. HCB is unintentionally generated as a by-product of the manufacture of perchloroethylene (also known as tetrachloroethylene, PER or PERC), carbon tetrachloride and, to some extent, trichloroethylene. For further information, see subsection I.B.7 (b) of the Pesticide POPs technical guidelines.

29. HCB is also unintentionally generated during the manufacture of some chemicals such as chloranil (2,3,5,6-tetrachloro-2,5-cyclohexadiene-1,4-dione), which is used as a fungicide. In addition, HCB is an intermediate in the synthesis of medicines and pesticides and is an oxidizing agent used in organic synthesis, particularly for dye intermediates. Concentrations in samples from China were in the  $\mu g \, per \, kg$  range (4-391  $\mu g \, per \, kg$ ) (Liu et al., 2012).

30. HCB may also be emitted from combustion-related sources when there is incomplete thermal decomposition of wastes resulting from the inappropriate operation of incinerators or from combustion at inadequate temperatures, especially in open burning of wastes, i.e., under the same conditions that can lead to the generation of PCDD and PCDF.

#### (d) PeCB

31. PeCB is an intermediate in the production of the fungicide pentachloronitrobenzene (PCNB, including but not limited to Quintozene). It may be produced as an impurity during the production of other chlorinated organic compounds.

32. PeCB is also unintentionally generated during the manufacture of some chemicals such as chloranil (2,3,5,6-tetrachloro-2,5-cyclohexadiene-1,4-dione). Concentrations in samples from China were in the same range as those for HCB (12-54  $\mu$ g *per* kg) (Liu et al., 2012).

33. PeCB may also be emitted from combustion-related sources where there is incomplete thermal decomposition of organic materials resulting from conditions known to generate PCDD and PCDF (UNEP, 2013a).

#### 3. Wastes

34. Wastes containing or contaminated with unintentionally generated PCDD, PCDF, PCB HCB, and PeCB can be found in:

- (a) Solids:
  - Contaminated soils and sediments (sites contaminated by the use of certain pesticides (see UNEP, 2013a), treated wood, open burning and the chemical industry);
  - (ii) Contaminated sludge (sludge containing industrially produced chemicals, solids and liquids);
  - (iii) Contaminated solid waste (paper, metal products, plastic, vehicle shredder fluff, painted objects, demolition waste, etc.);
  - (iv) Residues from air pollution control systems and residues left in combustion chambers such as sludge and bottom or fly ash resulting from high-temperature processes (incinerators, power plants, cement kilns, secondary metallurgical industry);
  - (v) Drained equipment with liquid residues (electrical, hydraulic or heat transfer equipment, internal combustion engines, pesticide application equipment);
  - (vi) Drained containers containing liquid residues from the equipment described in
    (v) above (independent of the materials of the containers, which could be waste oil drums, pesticide bottles or storage tanks), or absorbent materials;
  - (vii) Contaminated wood (PCB-contaminated or pesticide-impregnated wood);
  - (viii) Leather wastes;
- (b) Liquids:
  - (i) Contaminated oils (contained within or drained from internal combustion engines and from electrical, hydraulic or heat transfer equipment);
  - (ii) Certain pesticide formulations (herbicides, wood preservatives);
  - (iii) Mixed organic liquid wastes (paints, dyestuffs, oils, solvents);
  - (iv) Contaminated process water (industrial effluent, water from pollution control scrubbers and curtains, quench waters, sewage);
  - (v) Landfill leachates.

35. In addition, parts II and III of Annex C to the Stockholm Convention list source categories that have the potential to include wastes containing or contaminated with unintentionally produced PCDD, PCDF, PCB, HCB, or PeCB. See section B of chapter II below.

# **II.** Relevant provisions of the Basel and Stockholm conventions

#### A. Basel Convention

36. Article 1 ("Scope of the Convention") defines the types of waste that are subject to the Basel Convention. Subparagraph (a) of that Article sets forth a two-step process for determining whether a "waste" is a "hazardous waste" subject to the Convention: first, the waste must belong to any category contained in Annex I to the Convention ("Categories of wastes to be controlled"), and second, the waste must possess at least one of the characteristics listed in Annex III to the Convention ("List of hazardous characteristics").

37. Annexes I and II list some of the wastes that may contain or may be contaminated with unintentionally produced PCDD, PCDF, HCB, PCB or PeCB. These include:

- (a) Y5: Wastes from the manufacture, formulation and use of wood preserving chemicals;
- (b) Y6: Wastes from the production, formulation and use of organic solvents;
- (c) Y8: Waste mineral oils unfit for their originally intended use;
- (d) Y9: Waste oils/water, hydrocarbons/water mixtures, emulsions;

(e) Y10: Waste substances and articles containing or contaminated with polychlorinated biphenyls (PCBs) and/or polychlorinated terphenyls (PCTs) and/or polybrominated biphenyls (PBBs);

(f) Y12: Wastes from the production, formulation and use of inks, dyes, pigments, paints, lacquers, varnish;

- (g) Y18: Residues arising from industrial waste disposal operations;
- (h) Y39: Phenols; phenol compounds including chlorophenols;
- (i) Y41: Halogenated organic solvents;
- (j) Y42: Organic solvents excluding halogenated solvents;
- (k) Y43: Any congenor of polychlorinated dibenzo-furan;
- (l) Y44: Any congenor of polychlorinated dibenzo-p-dioxin;
- (m) Y45: Organohalogen compounds other than substances referred to in this Annex (e.g., Y39, Y41, Y42, Y43, Y44);
  - (n) Y47: Residues arising from the incineration of household wastes.

38. Wastes listed in Annex I are presumed to exhibit one or more Annex III hazardous characteristics, which may include H6.1 "Poisonous (Acute)", H11 "Toxic (Delayed or chronic)," or H12 "Ecotoxic", unless, through "national tests", they can be shown not to exhibit such characteristics. National tests may be useful for identifying a particular hazardous characteristic listed in Annex III until such time as the hazardous characteristic is fully defined. Guidance papers for Annex III hazardous characteristics H11, H12 and H13 were adopted on an interim basis by the Conference of the Parties to the Basel Convention at its sixth and seventh meetings.

39. List A of Annex VIII describes wastes that are "characterized as hazardous under Article 1, paragraph 1 (a) of this Convention" although "their designation on this Annex does not preclude the use of Annex III [hazard characteristics] to demonstrate that a waste is not hazardous" (Annex I, paragraph (b)). List B of Annex IX lists wastes that "will not be wastes covered by Article 1, paragraph 1 (a), of this Convention unless they contain Annex I material to an extent causing them to exhibit an Annex III characteristic." The following Annex VIII waste categories are applicable to unintentionally produced PCDD, PCDF, HCB, PCB or PeCB:

(a) A1180: Waste electrical and electronic assemblies or scrap<sup>2</sup> containing components such as accumulators and other batteries included on list A, mercury-switches, glass from cathode-ray tubes and other activated glass and PCBs-capacitors, or contaminated with Annex I constituents (e.g., cadmium, mercury, lead, polychlorinated biphenyl) to an extent that they possess any of the characteristics contained in Annex III (note the related entry on list B B1110)<sup>3</sup>;

(b) A3180: Wastes, substances and articles containing, consisting of or contaminated with polychlorinated biphenyl (PCB), polychlorinated terphenyl (PCT), polychlorinated naphthalene (PCN) or polybrominated biphenyl (PBB), or any other polybrominated analogues of these compounds, at a concentration level of 50 mg/kg or more<sup>4</sup>;

- (c) A4110: Wastes that contain, consist of or are contaminated with any of the following:
  - (i) Any congener of polychlorinated dibenzo-furan;
  - (ii) Any congener of polychlorinated dibenzo-p-dioxin.

40. List A of Annex VIII includes a number of wastes or waste categories that have the potential to contain or be contaminated with unintentionally produced PCDD, PCDF, HCB, PCB, or PeCB, including:

- (a) A1090: Ashes from the incineration of insulated copper wire;
- (b) A1100: Dusts and residues from gas cleaning systems of copper smelters;

<sup>&</sup>lt;sup>2</sup> This entry does not include scrap assemblies from electric power generation.

<sup>&</sup>lt;sup>3</sup> PCBs are at a concentration level of 50 mg/kg or more.

<sup>&</sup>lt;sup>4</sup> The 50 mg/kg level is considered to be an internationally practical level for all wastes. However, many countries have established lower levels (e.g., 20 mg/kg) for specific wastes in their regulations.

(c) A2040: Waste gypsum arising from chemical industry processes, when containing Annex I constituents to the extent that it exhibits an Annex III hazardous characteristic (note the related entry on list B B2080);

(d) A2060: Coal-fired power plant fly-ash containing Annex I substances in concentrations sufficient to exhibit Annex III characteristics (note the related entry on list B B2050);<sup>5</sup>

(e) A3020: Waste mineral oils unfit for their originally intended use;

(f) A3040: Waste thermal (heat transfer) fluids;

(g) A3070: Waste phenols, phenol compounds including chlorophenol in the form of liquids or sludges;

(h) A3120: Fluff – light fraction from shredding;

(i) A3150: Waste halogenated organic solvents;

(j) A3160: Waste halogenated or unhalogenated non-aqueous distillation residues arising from organic solvent recovery operations;

(k) A4040: Wastes from the manufacture, formulation and use of wood-preserving chemicals $^{6}$ ;

 A4070: Wastes from the production, formulation and use of inks, dyes, pigments, paints, lacquers, varnish excluding any such waste specified on list B (note the related entry on list B B4010);

(m) A4100: Wastes from industrial pollution control devices for cleaning of industrial off-gases but excluding such wastes specified on list B;

(n) A4150: Waste chemical substances arising from research and development or teaching activities which are not identified and/or are new and whose effects on human health and/or the environment are not known;

(o) A4160: Spent activated carbon not included on list B (note the related entry on list B B2060).<sup>7</sup>

41. List B of Annex IX to the Convention lists wastes that "will not be wastes covered by Article 1, paragraph 1 (a), of this Convention unless they contain Annex I material to an extent causing them to exhibit an Annex III characteristic." List B includes a number of wastes or waste categories that have the potential to contain or be contaminated with PCDD, PCDF, HCB, PCB or PeCB, including:

- (a) B1010: Metal and metal-alloy wastes in metallic, non-dispersible form, in particular:
  - Iron and steel scrap; and
  - Aluminium scrap.<sup>8</sup>

(b) B2080: Waste gypsum arising from industry process not included on list A (note the related entry on list A A2040);

(c) B2050: Coal-fired power plant fly-ash, not included on list A (note the related entry on list A A2060);

(d) B2060: Spent activated carbon not containing any Annex I constituents to the extent they exhibit Annex III characteristics, for example, carbon resulting from the treatment of potable water and processes of the food industry and vitamin production (note the related entry on list A A4160).

42. For further information, see section II.A of the general technical guidelines.

<sup>&</sup>lt;sup>5</sup> Category B2050 reads as follows: "Coal-fired power plant fly-ash, not included on list A."

<sup>&</sup>lt;sup>6</sup> This entry does not include wood treated with wood preserving chemicals.

<sup>&</sup>lt;sup>7</sup> Category B2060 reads as follows: "Spent activated carbon not containing any Annex I constituents to the extent they exhibit Annex III characteristics, for example, carbon resulting from the treatment of potable water and processes of the food industry and vitamin production."

<sup>&</sup>lt;sup>8</sup> For the full entry, see Annex IX to the Basel Convention.

#### B. Stockholm Convention

43. For POPs that are unintentionally generated as the result of human activity, Article 5 of the Convention ("Measures to reduce or eliminate releases from unintentional production") stipulates that each party must take "measures to reduce the total releases derived from anthropogenic sources of each of the chemicals listed in Annex C, with the goal of their continuing minimization and, where feasible, ultimate elimination". PCDD, PCDF, HCB, PCB or PeCB are listed in Part I of Annex C ("Unintentional production").

44. Part II of Annex C lists the following industrial source categories which have the potential for comparatively high levels of formation and release of unintentionally produced PCDD, PCDF, HCB, PCB or PeCB:

(a) Waste incinerators, including co-incinerators of municipal, hazardous or medical waste or of sewage sludge;

(b) Cement kilns firing hazardous waste;

(c) Production of pulp using elemental chlorine or chemicals generating elemental chlorine for bleaching;

- (d) The following thermal processes in the metallurgical industry:
  - (i) Secondary copper production;
  - (ii) Sinter plants in the iron and steel industry;
  - (iii) Secondary aluminium production;
  - (iv) Secondary zinc production.

45. Part III of Annex C lists source categories from which PCDD, PCDF, HCB, PCB or PeCB may also be unintentionally formed and released, including:

- (a) Open burning of waste, including burning of landfill sites;
- (b) Thermal processes in the metallurgical industry not mentioned in part II of Annex C;
- (c) Residential combustion sources;
- (d) Fossil-fuel-fired utility and industrial boilers;
- (e) Firing installations for wood and other biomass fuels;

(f) Specific chemical production processes releasing unintentionally formed persistent organic pollutants, especially production of chlorophenols and chloranil;

- (g) Crematoria;
- (h) Motor vehicles, particularly those burning leaded gasoline;
- (i) Destruction of animal carcasses;
- (j) Textile and leather dyeing (with chloranil) and finishing (with alkaline extraction);
- (k) Shredder plants for the treatment of end of life vehicles;
- (1) Smouldering of copper cables;
- (m) Waste oil refineries.

46. Part V of Annex C provides general guidance to parties on best available techniques (BAT) and best environmental practices (BEP) for preventing or reducing releases of unintentionally produced POPs. Specific guidance is contained in the *Guidelines on best available techniques and provisional guidance on best environmental practices relevant to Article 5 and Annex C of the Stockholm Convention on Persistent Organic Pollutants* (UNEP, 2007).

47. For further information, see section II.B of the general technical guidelines.

# III. Provisions of the Stockholm Convention to be addressed cooperatively with the Basel Convention

#### A. Low POP content

- 48. The following provisional definitions for low POP content should be applied:
  - (a) PCB: 50 mg/kg;<sup>9</sup>
  - (b) PCDD/PCDF: 15  $\mu$ g TEQ/kg<sup>10</sup>;
  - (c) HCB: 50 mg/kg;<sup>11</sup>
  - (d) PeCB: 50 mg/kg.<sup>12</sup>

49. The low POP content described in the Stockholm Convention is independent from the provisions on hazardous waste under the Basel Convention.

50. Wastes with a content of PCB, PCDD/PCDF, HCB or PeCB above the values specified in paragraph 48 must be disposed of in such a way that the POP content is destroyed or irreversibly transformed in accordance with the methods described in subsection IV.G.2. Otherwise, they may be disposed of in an environmentally sound manner when destruction or irreversible transformation does not represent the environmentally preferable option in accordance with the methods described in subsection IV.G.3.

51. Wastes with a content of PCB, PCDD/PCDF, HCB or PeCB at or below the values specified in paragraph 48 should be disposed of in accordance with the methods referred to in subsection IV.G.4 (disposal methods when the POP content is low) and taking into account subsections IV.I.1 and IV.I.2 (on higher and lower-risk situations, respectively).

52. For further information, see section III.A of the general technical guidelines.

#### B. Levels of destruction and irreversible transformation

53. For information, see section III.B of the general technical guidelines.

#### C. Methods that constitute environmentally sound disposal

54. For information, see section G of chapter IV below and section IV.G of the general technical guidelines.

# **IV.** Guidance on environmentally sound management (ESM)

#### A. General considerations

55. For information see section IV.A of the general technical guidelines.

#### **B.** Legislative and regulatory framework

56. Parties to the Basel and Stockholm conventions should examine their national strategies, policies, controls, standards and procedures to ensure that they are in agreement with the two conventions and with their obligations under them, including those that pertain to ESM of wastes consisting of, containing or contaminated with PCDD, PCDF, HCB, PCB or PeCB.

57. Elements of a regulatory framework applicable to substances listed in Annex C to the Convention should include measures to prevent the generation of wastes and to ensure the environmentally sound management. Measures and controls could include the following:

(a) Environmental protection legislation establishing a regulatory regime, setting release limits and mandating environmental quality criteria;

<sup>&</sup>lt;sup>9</sup> Determined in accordance with national or international methods and standards.

<sup>&</sup>lt;sup>10</sup> TEQ as referred to in Annex C, part IV, paragraph 2, to the Stockholm Convention, but only for PCDD and PCDF.

<sup>&</sup>lt;sup>11</sup> Ibid 9.

<sup>&</sup>lt;sup>12</sup> Ibid 9.

- (b) Transportation requirements for hazardous materials and waste;
- (c) Specifications for containers, equipment, bulk containers and storage sites;
- (d) Specification of acceptable analytical and sampling methods;
- (e) Requirements for waste management and disposal facilities;

(f) Definitions of hazardous waste conditions and criteria for the identification and classification of PCDD, PCDF, HCB, PCB or PeCB wastes as hazardous wastes;

(g) A general requirement for public notification and review of proposed government regulations, policy, certificates of approval, and licenses and inventory information and national releases/emissions data;

(h) Requirements for identification, assessment and remediation of contaminated sites;

(i) Requirements for health and safety protection of workers;

(j) Other potential legislative controls, as for waste prevention and minimization, inventory development and emergency response;

(k) Requirements for BAT/BEP to be used for destruction technologies for the POPs content of hazardous waste and for waste management facilities and landfills;

(1) Regulations imposing restrictions on open burning of the POP content of domestic waste;

(m) Regulations for ash disposal (including disposal of ashes from the burning of agricultural wastes); and

(n) Environmental assessment, including environmental impact assessment of new facilities for which emission limits for PCDD and PCDF may be a consideration.

58. For further information, see section IV.B of the general technical guidelines.

#### C. Waste prevention and minimization

59. Both the Basel and Stockholm conventions advocate waste prevention and minimization. With regard to PCDD/PCDF, the Stockholm Convention Expert Group on BAT and BEP (BAT/BEP expert group) has developed *Guidelines on best available techniques and provisional guidance on best environmental practices relevant to Article 5 and Annex C of the Stockholm Convention on Persistent Organic Pollutants* (UNEP, 2007) that apply to PCDD/PCDF and were adopted by the Conference of the Parties to the Stockholm Convention at its third meeting in 2007. The guidelines are currently being amended by the BAT/BEP expert group to include the new POPs that have been listed in Annex C to the Stockholm Convention since 2007.

60. It is likely that efforts to reduce the formation and release of PCDD and PCDF will also reduce the formation and release of unintentionally produced HCB, PCB or PeCB generated by the same processes.<sup>13</sup>

61. The mixing and blending of wastes with a content of PCB, PCDD/PCDF, HCB or PeCB above the values specified in paragraph 48 with other materials solely for the purpose of generating a mixture with a POP content at or below the values specified in paragraph 48 is not environmentally sound. Nevertheless, the mixing or blending of materials before waste treatment may be necessary in order to enable treatment or to optimize treatment efficiency.

62. For further information, see section IV.C of the general technical guidelines, the Toolkit for unintentional POPs (UNEP, 2013a) and the guidelines on BAT and provisional guidance on BEP referred to in paragraph 59 above (UNEP, 2007).

#### D. Identification of wastes

63. Article 6, paragraph 1 (a), of the Stockholm Convention requires each party to, *inter alia*, develop appropriate strategies for the identification of products and articles in use and wastes consisting of, containing or contaminated with POPs. It is recommended that parties consult the toolkit for unintentional POPs (UNEP, 2013a) for the identification of unintentional POPs in chemicals and consumer products.

<sup>&</sup>lt;sup>13</sup> For further information, see *Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs under Article 5 of the Stockholm Convention* (UNEP, 2013a).

64. For general information on identification of wastes, see section IV.D of the general technical guidelines.

#### 1. Identification

65. PCDD, PCDF, PCB, HCB and PeCB may be found in the following industries, equipment and locations (for details, see parts II and III of Annex C to the Stockholm Convention and paragraphs 44 and 45 of the present guidelines):

- (a) Waste incineration;
- (b) Cement kilns;
- (c) Pulp and paper production;
- (d) Metallurgical industries;
- (e) Fossil-fuel-fired utility and industrial boilers;
- (f) The production and use of certain pesticides;
- (g) Motor vehicle breaking and recovery;

(h) Drained equipment with liquid residues (electrical, hydraulic or heat transfer equipment, internal combustion engines, pesticide application equipment, shredders for end-of-life vehicles and other consumer goods);

(i) Drained containers with liquid residues (oil drums, plastic drums, pesticide bottles, storage tanks);

- (j) Painted objects, including wood, concrete and wallboard;
- (k) Mixed organic liquid wastes (paints, dyestuffs, oils, solvents);
- (1) Treated or contaminated wood (PCB-contaminated, pesticide-impregnated);
- (m) Contaminated soils, sediments, rock and mine aggregates;
- (n) Contaminated solid waste, including demolition waste;
- (o) Contaminated sludge;

(p) Contaminated oils (contained within or drained from internal combustion engines and electrical, hydraulic or heat transfer equipment);

(q) Contaminated process water (industrial effluent, water from pollution control scrubbers and curtains, quench waters, sewage);

(r) Open-air and other open burning of agricultural residues such as crop residues, stubble and bagasse; and

(s) Landfill leachates.

66. It should be noted that even experienced technical personnel may not be able to determine the nature of an effluent, substance, container or piece of equipment by its appearance or markings. Consequently, parties may find the information on production, use and types of waste provided in section I.B of the present guidelines useful in identifying PCDD, PCDF, HCB, PCB and PeCB.

#### 2. Inventories

67. According to Article 5, paragraph (a) (i), of the Stockholm Convention, action plans have to be developed for unintentionally produced POPs (i.e., chemicals listed in Annex C to the Convention) that should include an evaluation of current and projected releases of those chemicals, including the development and maintenance of source inventories and release estimates, taking into consideration the sources of unintentionally produced POPs listed in Annex C. Such inventories are important for identifying, quantifying and characterizing wastes.

68. The toolkit for unintentional POPs (UNEP, 2013a) constitutes the most comprehensive available compilation of emission factors for all relevant sources of the chemicals listed in Annex C to the Stockholm Convention. For countries where measurement data are limited, it enables the elaboration of source inventories and release estimates by using default emission factors. Since the formation of PCDD/PCDF is accompanied by releases of HCB, PeCB or PCB, releases of PCDD/PCDF are indicative of releases of the other chemicals listed in Annex C and can be used as a

basis for identifying and prioritizing sources of releases and for evaluating the efficacy of adopted measures for minimizing and ultimately eliminating releases of these chemicals.

#### E. Sampling, analysis and monitoring

69. For general information, see section IV.E of the general technical guidelines.

#### 1. Sampling

70. For information on sampling, see subsection IV.E.1 of the general technical guidelines. It should be noted that the presence of PCB, PeCB or HCB in a sample does not necessarily imply that the POP has been formed unintentionally. Only in the case of PCDD/PCDF can all concentrations be assumed to have been unintentionally formed.

71. Standard sampling procedures should be established and agreed upon before the start of the sampling campaign (both matrix- and POP-specific).

72. The types of matrices that are typically sampled for unintentionally generated PCDD, PCDF, HCB, PCB or PeCB include:

(a) Chemicals and pesticides that contain chlorine or whose synthesis process involved the use of chlorine, especially chlorophenol and its derivatives and other chlorinated aromatic compounds;

(b) Consumer goods known to be contaminated with PCDD or PCDF and in which PCB, HCB, and PeCB may be present, such as chemically bleached paper, textiles and leather;

(c) Stack emissions; these are typically analysed for PCDD/PCDF only; occasionally for dioxin-like PCB. Commonly used sampling methods include European standard 1948, EPA TO9. Indicator PCB, HCB, and PeCB are not regulated by any authority and there is no standard procedure for sampling.

#### 2. Analysis

73. In general, screening methods should be differentiated from confirmatory methods. Full analysis of unintentionally produced POPs is expensive, time consuming, and requires sophisticated equipment and experienced personnel. Capacity is therefore not always available. There are however screening methods available for these POPs that allow for a pre-selection of samples before undertaking confirmatory analysis with sophisticated equipment. Such screening may save time and costs.

74. Screening methods can be used to indicate the presence of POPs among other chemicals and are typically used for chemicals that require quite sophisticated instruments for analysis such as PCDD, PCDF or dioxin-like PCB. Bioanalytical screening methods to detect Ah-receptor binding have been developed, e.g. immunoassays or CALUX; these are sensitive enough to determine dioxin like-POPs at trace levels but also include other groups of chemicals. The European Union has set criteria for the use of bioanalytical methods in official controls for feed and food (EU 2009, EU 2014).

75. In chemical-analytical laboratories, simple clean-up steps followed by GC-ECD separation and detection of the main peak can be used as well in screening steps.

76. All screenings methods should not generate false negatives. If not otherwise agreed, all samples resulting positive should undergo confirmatory measurements for final quantification.

77. Confirmatory methods for the unintentionally produced POPs, include separation of the POPs on a capillary gas chromatographic column followed by detector to identify and quantify. As stated in the the *Guidance for the global monitoring plan for persistent organic pollutants* (UNEP, 2015f), all methods should apply internal standards for identification and quantification.

78. For information on analytical methods for the determination of unintentional POPs, see annex II to the present guidelines.

79. Analysis for PCDD and PCDF and also for HCB, PCB or PeCB as unintentionally produced POPs differs from the analysis of intentionally produced POPs insofar as, typically, the concentrations to be determined are many orders of magnitude lower than for other POPs. This requires special expertise and equipment; for example, only mass-selective detectors are acceptable for quantification.

80. Determination of unintentionally produced POPs other than the dioxin-like POPs, e.g., HCB, PCB and PeCB, since they are also intentionally produced POPs routinely are not analysed by the

same sophisticated equipment like the PCDD/PCDF and dioxin-like PCB. Further, the six most common PCB (indicator PCB), HCB and PeCB are not found in the same fraction after clean-up as the PCDD, PCDF and dioxin-like. HCB and PeCB are analysed together with POPs pesticides using capillary gas chromatography in combination with electron capture or preferred low resolution mass-selective detectors. For details on the analysis of PCB please refer to the PCBs technical guidelines and the Pesticides technical guidelines for HCB and PeCB.

81. For further information on analysis, see subsection IV.E.2 of the general technical guidelines.

#### 3. Monitoring

82. Monitoring programmes should be implemented for facilities managing wastes containing or contaminated with PCDD, PCDF, HCB, PCB or PeCB. For further information, see subsection IV.E.3 of the general technical guidelines.

#### F. Handling, collection, packaging, labelling, transportation and storage

83. For general information on handling, collection, packaging, labelling, transportation and storage, see the first two paragraphs of section F of the general technical guidelines.

#### 1. Handling

84. For information, see subsection IV.F.1 of the general technical guidelines.

#### 2. Collection

85. A significant fraction of total national inventories of wastes containing or contaminated with PCDD, PCDF, HCB, PCB or PeCB may not be adequately identified.

86. Collection costs may be prohibitive, and national, regional and municipal governments should consider establishing schemes for the collection and removal of wastes containing or contaminated with PCDD, PCDF, HCB, PCB or PeCB (see subsection IV.I.1 below, on "higher-risk situations").

87. Collection operations and collection depots for wastes containing or contaminated with PCDD, PCDF, HCB, PCB or PeCB should ensure that such wastes are handled and stored separately from all other wastes.

88. It is imperative that collection depots do not become long-term storage facilities for wastes containing or contaminated with PCDD, PCDF, HCB, PCB or PeCB.

89. For further information, see subsection IV.F.2 of the general technical guidelines.

#### 3. Packaging

90. Wastes containing or contaminated with PCDD, PCDF, HCB, PCB or PeCB should be properly packaged before storage or transport:

(a) Liquid wastes should be placed in double-bung steel drums or other approved containers;

(b) Regulations governing the transport of hazardous materials often require the use of containers that meet certain specifications (e.g., 16-gauge, made of steel, internally coated with epoxy). Containers used for storage should meet such specifications given that they may be transported in the future;

(c) Large, drained equipment may be stored as is or may be placed inside large containers (overpack drums) or heavy plastic wraps if leakage is a concern;

(d) Small pieces of equipment, whether drained or not, should be placed in drums with an absorbent material, where appropriate, to prevent excessive movement of container contents and enable any free liquids/spills to be absorbed. Numerous small pieces of equipment may be placed in the same drum so long as an adequate amount of absorbent material is present in the drum. Loose absorbents may be purchased from safety suppliers;

(e) Drums and equipment may be placed on pallets for movement by forklift truck and for storage. Drums and equipment should be strapped to the pallets before they are moved.

91. For further information, see subsection IV.F.3 of the general technical guidelines.

#### 4. Labelling

92. Every container carrying wastes containing or contaminated with PCDD, PCDF, HCB, PCB or PeCB should be clearly labelled with a hazard-warning label and a label providing details of the container. Such details should include the contents of the container (exact weight or volume of a liquid, type of waste carried), the name of the site from which the wastes originated so as to allow their traceability and, if applicable, the date of waste repackaging and the name and telephone number of the person responsible for the repackaging operation.

93. For further information, see subsection IV.F.4 of the general technical guidelines.

#### 5. Transportation

94. For information, see subsection IV.F.5 of the general technical guidelines.

#### 6. Storage

95. The storage procedures for PCDD, PCDF, HCB, PCB or PeCB wastes should be similar to those for other POPs, as their properties and toxicity are broadly similar to those of other POPs.

96. For further information, see subsection IV.F.6 of the general technical guidelines.

#### G. Environmentally sound disposal

#### 1. Pre-treatment

97. Techniques which separate unintentionally produced POPs from the waste matrix are of particular relevance. Those techniques include solvent washing and thermal desorption as, in most cases, wastes contaminated by unintentionally produced POPs are solid substances such as fly ashes and other residues from off-gas cleaning. Oil-water separation may also be important.

98. For further information, see subsection IV.G.1 of the general technical guidelines.

#### 2. Destruction and irreversible transformation methods

99. For available destruction and irreversible transformation methods, see subsection IV.G.2 of the general technical guidelines.

# **3.** Other disposal methods when neither destruction nor irreversible transformation is the environmentally preferable option

100. For information, see subsection IV.G.3 of the general technical guidelines.

#### 4. Other disposal methods when the POP content is low

101. For information, see subsection IV.G.4 of the general technical guidelines.

#### H. Remediation of contaminated sites

102. For information, see section IV.H of the general technical guidelines.

#### I. Health and safety

103. For information, see section IV.I of the general technical guidelines.

#### 1. Higher-risk situations

104. Unintentionally produced HCB, PCB or PeCB are not covered under this subsection because they are very unlikely to be generated in concentrations or volumes greater than those from intentional production.

105. For further information on higher-risk situations, see subsection IV.I.1 of the general technical guidelines. Potential higher-risk situations specific to PCDD and PCDF may include:

- (a) Sites with residues from air pollution control systems;
- (b) Sites with graphite electrodes;

(c) Production and application sites of chlorinated phenols and its derivatives and sludges and other wastes from processes using elemental chlorine;

#### (d) Consumption of dioxin-contaminated food.

106. As any PCB-containing site will also have high concentrations of PCDF, see also section IV.I of the PCBs technical guidelines.

#### 2. Lower-risk situations

107. For information on lower-risk situations, see subsection IV.I.2 of the general technical guidelines. Lower-risk situations specific to PCDD and PCDF may include facilities where unintentionally produced POPs occur in low concentrations and low volumes.

#### J. Emergency response

108. Emergency response plans should be in place for wastes containing or contaminated with PCDD, PCDF, HCB, PCB or PeCB in storage, in transport or at disposal sites. Further information on emergency response plans can be found in section IV.J of the general technical guidelines.

## K. Public participation

109. Parties to the Basel and Stockholm conventions should have open public participation processes. For further information, see section IV.K of the general technical guidelines.

# Annex I to the technical guidelines

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UNEP, 2015. Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with polychlorinated biphenyls, polychlorinated terphenyls or polybrominated biphenyls including hexabromobiphenyl. [PCBs technical guidelines]

UNEP, 2015a. Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with the pesticides aldrin, alpha hexachlorocyclohexane, beta hexachlorocyclohexane, chlordane, chlordecone, dieldrin, endrin, heptachlor, hexachlorobenzene, lindane, mirex, pentachlorobenzene, perfluorooctane sulfonic acid, technical endosulfan and its related isomers or toxaphene or with hexachlorobenzene as an industrial chemical. [Pesticide POPs technical guidelines]

UNEP, 2015b. Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride.

UNEP, 2015c. Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with hexabromodiphenyl ether and heptabromodiphenyl ether or tetrabromodiphenyl ether and pentabromodiphenyl ether.

UNEP, 2015d. Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with hexabromocyclododecane.

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# Annex II to the technical guidelines

# Analytical methods for the determination of unintentional POPs

The present annex contains references applicable to PCDD and PCDF only, since the other unintentionally produced POPs, i.e., PCBs, HCB and PeCB, are covered by the Pesticide POPs technical guidelines (UNEP, 2015a) and the PCBs technical guidelines (UNEP, 2015).

#### 1. ISO methods

1. ISO methods are available for a fee from www.iso.org and are globally applicable. The published methods listed below, which were valid as of August 2014, may be retrieved.

Standard	Language(s)
ISO 17858:2007 Water quality Determination of dioxin-like polychlorinated biphenyls Method using gas	English
chromatography/mass spectrometry	
Edition: 1, <u>TC 147/SC 2</u> , ICS: <u>13.060.50</u> Document available as of: 12.02.2007	
<u>ISO 16000-13:2008</u>	English,
Indoor air Part 13: Determination of total (gas and particle-phase) polychlorinated dioxin- like biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDDs/PCDFs) Collection on sorbent-backed filters	French
Edition: 1, <u>TC 146/SC 6</u> , ICS: <u>13.040.20</u>	
Document available as of: 29.10.2008	
<u>ISO 16000-14:2009</u>	English,
Indoor air Part 14: Determination of total (gas and particle-phase) polychlorinated dioxin- like biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDDs/PCDFs) Extraction, clean-up and analysis by high-resolution gas chromatography and mass spectrometry	French
Edition: 1, <u>TC 146/SC 6, ICS: 13.040.20</u>	
Document available as of: 15.05.2009	
ISO 18073:2004 Water quality Determination of tetra- to octa-chlorinated dioxins and furans Method using isotope dilution HRGC/HRMS	English, French
ISO 18073:2004 specifies a method for the determination of tetra- to octa-chlorinated dibenzo- p-dioxins (PCDDs) and dibenzofurans (PCDFs) in waters and waste waters (containing less than 1 % by mass solids) using high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS). The minimum levels (MLs) at which the PCDDs/PCDFs can currently be determined with no interferences present are specified. This method is "performance based". The analyst is permitted to modify the method to overcome interferences or lower the cost of measurements, provided that all performance criteria are met. The requirements for establishing method equivalency are given. Edition: 1, TC 147/SC 2, ICS: 13.060.50	

# 2. CEN methods

2. Methods can be obtained against a fee at the following website: www.cen.eu. They are applicable to European Union Member States. The following published methods are available:

Standard reference	Title	Directive (OJEU citation <sup>*</sup> )
CEN/TC 264 - A	ir quality	
<u>EN 1948-1:2006</u>	Stationary source emissions - Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs - Part 1: Sampling of PCDDs/PCDFs	94/67/EC (No.) 89/429/EEC (No.) 89/369/EEC (No.)
<u>EN 1948-2:2006</u>	Stationary source emissions - Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs - Part 2: Extraction and clean-up of PCDDs/PCDFs	94/67/EC (No.) 89/429/EEC (No.) 89/369/EEC (No.)
<u>EN 1948-3:2006</u>	Stationary source emissions - Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs - Part 3: Identification and quantification of PCDDs/PCDFs	94/67/EC (No.) 89/429/EEC (No.) 89/369/EEC (No.)
<u>EN 1948-4:2010</u>	Stationary source emissions - Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs - Part 4: Sampling and analysis of dioxin-like PCBs	-
<u>EN ISO 16000-</u> <u>12:2008</u>	Indoor air - Part 12: Sampling strategy for polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polycyclic aromatic hydrocarbons (PAHs) (ISO 16000-12:2008)	89/106/EEC (No)

\* Official Journal of the European Union, accessible in languages from: http://eur-lex.europa.eu/

#### 3. United States of America

3. The Office of Solid Waste of the U.S. Environmental Protection Agency has produced various methods that can be retrieved from

http://www.epa.gov/waste/hazard/testmethods/sw846/online/index.htm. Several series of wastewater methods have been published under 40 CFR Part 136, including the 200, 600 and 1600 series. All series are available at http://water.epa.gov/scitech/methods/cwa/methods\_index.cfm. In addition to wastewater methods, the EPA has produced methods for air (300 series, MACT standards), drinking water (500 series) and solid waste (8000 series).

Method (including updates)	Title
8280, 8280A, 8280B	The Analysis of Polychlorinated Dibenzo- <i>p</i> -Dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/Low Resolution Mass Spectrometry (HRGC/LRMS)
8290, 8290A	SW846 Method 8290, "Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS)", Revision 0, November 1992. Available at: http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/8290a.pdf
0023A (Up. III)	Sampling Method for Polychlorinated Dibenzo- <i>p</i> -Dioxins and Polychlorinated Dibenzofuran Emissions from Stationary Sources (Note: This method is a revision of Method 23, 40 CFR Part 60.)
	Method 23 - Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Municipal Waste Combustors. Available at:
	http://www.epa.gov/ttn/emc/promgate/m-23.pdf
613	Methods for organic chemical analysis of municipal and industrial wastewater method 613—2,3,7,8-Tetrachlorodibenzo-p-dioxin
	EPA Solid Waste. Available at:

Method (including updates)	Title
	http://www.epa.gov/waterscience/methods/method/organics/613.pdf
ТО-9	Determination Of Polychlorinated, Polybrominated And Brominated/Chlorinated Dibenzo-p-Dioxins And Dibenzofurans In Ambient Air
1613B	Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, October 1994; EPA Office of Water
	Isomer-specific determination of the 2,3,7,8-substituted, tetra- through octa-chlorinated, dibenzo- <i>p</i> -dioxins and dibenzofurans in aqueous, solid, and tissue matrices by isotope dilution, high resolution capillary column gas chromatography (HRGC)/high resolution mass spectrometry (HRMS) It is approved by Federal Register 1997 under Clean Water Act and applicable to (waste)water, soil, sediment, biota/ tissues
	http://www.epa.gov/ost/methods/1613.pdf, Tetra-through Octa-Chlorinated Dioxins and Furans by Isotope Dilution High Resolution Gas Chromatography/High Resolution Mass Spectrometry Revision B
23	Method 23 - Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Municipal Waste Combustors. Available at: <u>http://www.epa.gov/ttn/emc/promgate/m-23.pdf</u>

#### 4. China

4. China's national standards for environmental monitoring can be retrieved from http://kjs.mep.gov.cn/hjbhbz/ and are available in Chinese only; an unofficial translation of the titles of the standards is provided below.

5. The Chinese national standards for PCDD/PCDF analysis (HJ-77.1-2008, HJ-77.2-2008, HJ-77.3-2008, HJ-77.4-2008) are a mix of international methods, including EN 1948, EPA methods 1613, 8290 and 23A and Japanese Industrial Standard (JIS) methods K0311 and K0312, but they most resemble EN 1948. The Chinese national standards for PAH analysis are different from those of other counties; however, the target 16 PAHs in HJ478-2009 are the same chemicals as those covered by EPA method 610.

Standard reference	Title
HJ-77.1-2008	Water quality - Determination of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) by isotope dilution HRGC-HRMS
	Document available as of: 31.12.2008
HJ-77.2-2008	Ambient air and waste gas - Determination of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) by isotope dilution HRGC-HRMS
	Document available as of: 31.12.2008
HJ-77.3-2008	Solid waste - Determination of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) by isotope dilution HRGC-HRMS
	Document available as of: 31.12.2008
HJ-77.4-2008	Soil and sediment - Determination of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) by isotope dilution HRGC-HRMS
	Document available as of: 31.12.2008

#### 5. Japan

#### a) JIS K 0311:2005

6. JIS K 0311:2005 standard serves to determine tetra-through octachlorodibenzo-p-dioxins, tetrathrough octachlorodibenzofurans and dioxin-like polychlorinatedbiphenyls in stationary source emissions.

7. The standard specifies the method of analysis for tetra-through octachlorodibenzo-para-dioxins, tetra-through octachlorodibenzofurans and dioxin-like PCBs in exhaust gas that are generated by combustion and chemical reactions and are discharged to flues, stacks or ducts in stationary source emissions using gas chromatography instruments coupled with mass spectrometers.

8. Date Established: 1999-09-20, Date Revised: 2005-06-20, Date Published: 2005-06-20; 2008-01-20 (Revised).

9. The standard is available in Japanese and English and can be obtained for a fee from http://www.webstore.jsa.or.jp/webstore/Com/FlowControl.jsp?lang=en&bunsyoId=JIS+K+0311%3A20 05&dantaiCd=JIS&status=1&pageNo=0.

#### 6. Germany

Method	Title / Description
DIN ISO 16000-13	Indoor air - Part 13: Determination of total (gas and particle-phase) polychlorinated dioxin-like biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDDs/PCDFs) - Collection on sorbent-backed filters (ISO 16000-13:2008)
	Published in 2010-03; available in German, English and French.
DIN ISO 16000-14	Indoor air — Part 14: Determination of total (gas and particle-phase) polychlorinated dioxin-like biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDDs/PCDFs) — Extraction, clean-up and analysis by high-resolution gas chromatography and mass spectrometry.
	Published on 2009-05-15; available in German, English and French.
DIN EN ISO 16000-12	Indoor air - Part 12: Sampling strategy for polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polycyclic aromatic hydrocarbons (PAHs) (ISO 16000-12:2008)
	Published in 2008-08; available in German, English and French.
DIN ISO 16000-13	Indoor air - Part 13: Determination of total (gas and particle-phase) polychlorinated dioxin-like biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDDs/PCDFs) - Collection on sorbent-backed filters (ISO 16000-13:2008)
	Published in 2010-03; available in German, English and French.
VDI 3498 Blatt 1	Ambient air measurement - Indoor air measurement - Measurement of polychlorinated dibenzo-p-dioxins and dibenzofurans; Method using large filters
	Published in 2002-07; available in German and English.
VDI 3498 Blatt 2	Ambient air measurement - Indoor air measurement - Measurement of polychlorinated dibenzo-p-dioxins and dibenzofurans; Method using small filters
	Published in 2002-07; available in German and English
DIN38414-20	German standard methods for the examination of water, wastewater and sludge - Sludge and sediments (group S) - Part 20: Determination of 6 polychlorinated biphenyls (PCB) (S 20)
	Published in 1996-01; available in German and English.

#### 7. Canada

Report EPS 1/RM/19, February 1992 Reference Method for the Determination of Polychlorinated Dibenzo-para-dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) in Pulp and Paper Mill Effluents. Available at: http://www.ec.gc.ca/lcpe-cepa/default.asp?lang=En&n=89496F4E-1.

Report EPS 1/RM/23, October 1992

Internal Quality Assurance Requirements for the Analysis of Dioxins in Environmental Samples. Available at: http://www.ec.gc.ca/lcpe-cepa/default.asp?lang=En&n=5ED227EE-1.