HORIZONTAL STANDARDISATION FOR SOIL, SEDIMENT, SLUDGE AND BIO-WASTE

Report of the final desk study
on the determination of PCDD/F and DL-PCB

for the European project HORIZONTAL

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CONTENTS

1 OVERVIEW

1.1 Introduction

The European project HORIZONTAL is focused on the standardisation of analytical methods for the analyses of various inorganic and organic contaminants in soil, sludge and bio waste. During the preparation of the project, several desk studies have been started to elaborate the possibility of horizontal standardisation on specific subjects. One of these subjects was the horizontal standardisation of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans (PCDD/F) together with the Dioxinlike Polychlorinated Biphenyls (DL-PCB).

At European level only a standard method for the analysis of PCDD/F in emissions from stationary sources (EN 1948) exists, which is now in re-evaluation and will be extended to DL-PCB. At International level there exist standards for the analysis of PCDD/F and DL-PCB in water (ISO/DIS 18073 and ISO/DIS 17858). Several standards and method recommendations for the analysis of PCDD/F in various solid matrices exist at national level.

This report describes the results of the desk study on the issue of PCDD/F and dioxinlike PCB. The aim of this desk study was to review the relevant scientific literature and existing analytical methods described in national and international standards and method recommendations. The critical review clearly showed that it is reasonable to establish a horizontal standard for the analysis of PCDD/F and DL-PCB in soil, sludge and bio waste samples. The review also showed that the future horizontal standard could easily be extended to various environmental solid materials, e.g. sediment, minerals, vegetation and compositions thereof.

An overview on the issue of PCDD/F and DL-PCB and a proposal of the structure of the future standard is given in this study.

1.2 Sources

The chlorinated dioxins and furans are generated as by-products from various combustion processes. These can include waste incineration (such as municipal solid waste, sewage sludge, medical waste, and hazardous wastes), burning of various fuels (such as coal, wood, and petroleum products), and poorly or uncontrolled combustion sources (open burning of wastes). Currently, it is believed that PCDD/PCDFs emissions associated with human incineration and combustion activities are the predominant environmental source. Emissions from incinerator sources vary greatly and depend on management practices and applied technologies.

Although Dioxins can be considered as anthropogenic contaminant, recent studies showed that there is also a natural formation of PCDD/F possible. Recent studies suggest that PCDD/PCDFs can be formed under certain environmental conditions (e.g., composting) from the action of micro organisms on chlorinated phenolic compounds. Another pathway of natural production of PCDD/F is incomplete combustion of organic material by forest fires or volcanic activity. Similarly, PCDD/PCDFs have been reported to be formed during photolysis of highly chlorinated phenols.

PCDD/PCDFs also have been detected at low concentrations in cigarette smoke, home-heating systems, and exhaust from cars running on leaded gasoline or unleaded gasoline, and diesel fuel.

Burning of many materials that may contain chlorine, such as plastics, wood treated with pentachlorophenol (PCP), pesticide-treated wastes, other polychlorinated chemicals (polychlorinated biphenyls or PCBs), and even bleached paper can produce dioxins.

PCDD/PCDFs can be formed during various types of primary and secondary metals operations including iron ore sintering, steel production, and scrap metal recovery.

Chemical manufacturing of chlorinated phenols (e.g., pentachlorophenol-PCP), polychlorinated biphenyls (PCBs), the phenoxy herbicides (e.g., 2,4,5-T), chlorinated benzenes, chlorinated aliphatic compounds (e.g., ethylene dichloride), chlorinated catalysts and halogenated diphenyl ethers are known to generate PCDD/PCDFs. 2,3,7,8-TCDD is a by-product formed during the manufacture of 2,4,5-trichlorophenol (2,4,5-TCP) what was used to produce the bactericide hexachlorophene and the herbicide, 2,4,5-trichlorophenoxyacetic acid (2,4,5-T). Various formulations of 2,4,5-T have been used extensively for weed control and 2,4,5-T was a component of Agent Orange, which was used extensively by the U.S. military in the Vietnam War. In most industrialized countries the use of products contaminated with PCDD/PCDFs has been greatly reduced.

Industrial and municipal processes in which naturally occurring phenolic compounds are chlorinated, e.g. chlorine bleaching process used by pulp and paper mills, can produce dioxins.

1.3 Environmental Levels

Soil contamination with PCDD/F and DL-PCB occurs mainly by atmospheric deposition, air transport of soil particles from contaminated sites, deposition of sediments caused by floods and by soil treatment processes. The most important soil treatment process in this context is fertilization of agricultural used soil with sewage sludge. Typical contamination levels of soils from rural areas are in the range from 1 to 10 ng TEQ /kg. In conurbations soil contaminations can go up to several hundred ng TEQ /kg and at contaminated sites concentrations can go up to several thousands ng TEQ /kg (H.Fiedler, K.Fricke, H.Vogtmann, 1994)

For sewage sludge from European regions average PCDD/F concentration levels can be expected around 20 ng TEQ /kg DM. A comprehensive study about the situation of municipal sewage sludge in Austria, carried out by the Umweltbundesamt Wien, showed average concentrations of 14,5 ng TEQ /kg DM. The maximum concentration of the samples investigated was 38,1 ng TEQ /kg DM. For the contamination of sewage sludge with PCDD/F two major pathways can be assumed. PCDD/F can be washed out from the atmosphere by rain and can be deposited to sealed surfaces, e.g. roads. Runoff of these surfaces will enter the sewage treatment plants. The second pathway is the transport of PCDD/F by water through sewers from households and industries (S.Scharf, M.Schneider, G.Zethner, 1997).

Just as in other media dioxins and furans as anthropogenic compounds are also detectable in organic waste. In a resent survey, carried out by the Umweltbundesamt Wien, the quality of compost from divided waste collection was investigated. The results of this study showed a maximum value of 86,8 ng I-TEQ/kg in one compost sample and a sample median of 6.43 ng I-TEQ/kg dry matter. Compost from bio waste, containing contaminated materials like treated wood, chipboards as well as leaves and grass from particularly contaminated sites can have much higher concentrations (G.Zethner, B.Götz, F.Amlinger, 2000).

1.4 Fate

Gas-phase PCDD/PCDFs released to the atmosphere may be degraded by reaction with hydroxyl radicals and direct photolysis. It has been estimated that 20 to 60% of 2,3,7,8-TCDD in the air is in the vapour phase. It reacts with photochemically produced hydroxyl radicals in air at an estimated half-life rate of 8.3 days; direct photolysis of gas-phase TCDD may occur at a faster rate than hydroxyl radical reaction.

Particulate-phase PCDD/PCDFs may be physically removed from air by wet and dry deposition. The larger particles will be deposited close to the emission source, while very small particles may be transported longer distances. Some of the lower chlorinated PCDDs (DCDD, TrCDD, and some of the TCDDs) may vaporize from the particles (and soil or water surfaces) and be transported long distances in the atmosphere. An ultimate environmental sink of airborne particulates may be sediments of the earth's surface waters.

PCDD/PCDFs released to water will be strongly associated with sediments and suspended material. Water transport of TCDD is limited since its solubility in water is only 0.2 ppb. Dioxins near the water's surface may experience significant photo degradation. Volatilization from the water column may be important, but adsorption to sediment will limit the overall rate by which dioxins are removed from water. The persistence half-life of 2,3,7,8-TCDD in lakes has been estimated to be in excess of 1.5 yr. Bioconcentration in aquatic organisms has been demonstrated.

Some of the CDDs deposited on or near the water surface will be broken down by sunlight. A very small portion of the total PCDD/PCDFs in water will evaporate to air. Because PCDD/PCDFs do not dissolve easily in water, most of the PCDD/PCDFs in water will attach strongly to small particles of soil or organic matter and eventually settle to the bottom. PCDD/PCDFs may also attach to microscopic plants and animals (plankton) which are eaten by larger animals, which are in turn eaten by even larger animals. This is called a food chain. Concentrations of chemicals such as the most toxic, 2,3,7,8-chlorine substituted dioxins, which are difficult for the animals to break down, usually increase at each step in the food chain. This biomagnification process is the reason why undetectable levels of CDDs in water can result in measurable concentrations in aquatic animals.

PCDD/PCDFs deposited on land bind strongly to the soil, and therefore are not likely to contaminate groundwater by leaching processes. Presence of other chemical pollutants in contaminated soils (e.g., oil spills), may dissolve PCDD/PCDFs, making it easier to move through the soil. Soil erosion and surface runoff can also transport PCDD/PCDFs into surface waters. Photodegradation on terrestrial surfaces may be an important transformation process. Volatilization from soil surfaces during warm, summer months may be a major mechanism by which TCDD is removed from soil. Volatilization during cold, winter months or from soil depths several centimetres below the boundary layer is extremely slow. The persistence half-life of 2,3,7,8-TCDD on soil surfaces may vary from less than 1 yr to 3 yrs, but half-lives in soil interiors may be as long as 12 years.

Although certain types of soil bacteria and fungus can break many PCDD/PCDFs down very slowly, the most toxic 2,3,7,8-TCDD is generally resistant to biodegradation.

Plants take up only very small amounts of dioxins with their roots. Most of the PCDD/PCDFs found on the parts of plants above the ground probably come from air and dust and/or previous use of dioxin containing pesticides or herbicides. Animals (such as cattle) feeding on the plants may accumulate PCDD/PCDF/dioxin like PCBs in their body tissues (meat) and milk.

1.5 2,3,7,8-Tetrachlorodibenzo-p-dioxin Toxic Equivalents

2,3,7,8-Tetrachlorodibenzo-p-dioxin is considered the most potent congener of the polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) families of compounds. Potency of PCDD and PCDF congeners correlates with the binding affinity to the cytosolic Ah receptor.

Toxic equivalents (TEFs) of PCDD, PCDF and dioxin-like PCB congeners have been developed and introduced to describe the cumulative toxicity of complex mixtures of these compounds, when encountered in the environment. TEFs are calculated relative to the most potent congener, 2,3,7,8-tetrachlorodibenzo-p-dioxin.

In the 1980s various models were developed for risk assessment of complex mixtures of PCDD/PCDF by several institutions (WHO, Nordic countries, US EPA, NATO CCMS). A feature all these models have in common is that a selected number of congeners is assigned so-called Toxic Equivalency Factors (TEFs) which are to express a toxicity equivalent to that of 2,3,7,8-TCDD. The measured concentrations of these selected congeners are each multiplied by a congener specific equivalency factor to calculate the toxic equivalent (TEQ) concentration. The TEQ concentrations of the various congeners are subsequently summed up to give the overall TEQ concentration of the medium investigated. In Table 1 some TEFs developed in the 1980s are summarized (Environmental Health Criteria 88, 1989).

The TEFs are based on acute toxicity values from in vivo and in vitro studies. This approach is based on the evidence that there is a common, receptor-mediated mechanism of action for these compounds.

However, the TEF approach has its limitations due to a number of simplifications. One of the limitations of the use of the TEF methodology in risk assessment of complex environmental mixtures is that fate and distribution of PCDDs, PCDFs and PCBs are not necessarily related to their TEF. Although the scientific basis cannot be considered as solid, the TEF approach has been developed as an administrative tool and allows the conversion of quantitative analytical data for individual PCDD/PCDF congeners into a single Toxic Equivalent (TEQ):

The above mentioned NATO-CCMS research groups selected 7 compounds from the Polychlorinated Dibenzo-p-dioxins and 10 compounds from the Polychlorinated Dibenzofurans to represent the 210 individual congeners, and assessed them by International Toxic Equivalency Factors (I-TEFs). At the European level the NATO-CCMS assessment method has been taken into account in the formulation of the EU waste incineration directive (NATO/CCMS, 1988).

In 1997 a WHO-ECEH and IPCS working group re-evaluated the I-TEFs and established a new scheme. The WHO re-evaluation chose also to include 12 non-ortho and mono-ortho-substituted polychlorinated biphenyls (PCB) into the TEF scheme for dioxin-like toxicity. The NATO and the WHO schemes are found in the Table 2 . (WHO ECEH/IPCS, 1998).

From the dioxins, 1,2,3,7,8-PeCDD was re-evaluated with a TEF of 1 (NATO-CCMS value: 0.5). In contrast, the TEFS for OCDD and OCDF were reduced by a factor of 10, to 0.0001 (NATO-CCMS value: 0.001) (B. Johnke et al, 2003).

TEF values for individual congeners in combination with their chemical concentration can be used to calculate the total TCDD toxic equivalents concentration (TEQs) contributed by all dioxin-like congeners in the mixture using the following equation which assumes does additivity:

$$TEQ = \Sigma(PCDD_i \text{ x } TEF_i) + \Sigma(PCDF_i \text{ x } TEF_i) + \Sigma(PCB_i \text{ x } TEF_i)$$

The majority of studies assessing the manner in which binary and complex mixtures of dioxin-like PCDD, PCDF and PCB interact to cause toxicity have demonstrated that the interaction does not deviate significantly from dose additivity. This includes investigations conducted in various classes of vertebrates (fish, birds and mammals) and on environmental relevant mixtures. TEFs for dioxin-like compounds apply only to AhR-mediated responses. The criteria for including a compound in the TEF scheme for dioxin-like compounds are that the compounds must:

Show a structural relationship to the PCDDs and PCDFs

Bind to the Ah receptor

Elicit Ah receptor-mediated biochemical and toxic responses

Be persistent and accumulate in the food chain

To reassess the TEFs for mammals a WHO expert group recently applied a tiered approach in which results of animal toxicity studies, especially those involving (sub)chronic exposure, were given significantly more weight than results of in vitro or biochemical studies (D. Bockley-Golder, 1999).

Recognizing that certain uncertainties exist in the use of the TEF concept for human risk assessment, pragmatically it remains the most feasible approach.

Table 1: Toxic Equivalency Factors (Environmental Health Criteria 88, 1989; B. Johnke et al, 2003)

Compound	Olie et al. 1983	Switzerland 1982	Germany 1985	Denmark 1984	US EPA 1987	NATO 1990
Dibenzo-p-dioxins						
TetraCDD-2,3,7,8	1,0	1,0	1,0	1,0	1,0	1,0
PentaCDD 1,2,3,7,8	0,1			0,01		0,5
HexaCDD 1,2,3,4,7,8				0,1		0,1
HexaCDD 1,2,3,7,8,9				0,01		0,1
HexaCDD 1,2,3,6,7,8				0,01		0,1
HeptaCDD 1,2,3,4,6,7,8				0,01		0,001
OctaCDD			0,001			0,001
Dibenzofurans						
TetraCDF-2,3,7,8	0,1	0,1	0,1	0,1	0,1	0,1
PentaCDF-2,3,4,7,8				0,2		0,5
PentaCDF-1,2,3,7,8				0,2		0,05
HexaCDF-1,2,3,4,7,8				0,2		0,1
HexaCDF-1,2,3,7,8,9						0,1
HexaCDF-1,2,3,6,7,8				0,05		0,1
HexaCDF-2,3,4,6,7,8				0,1		0,1
HeptaCDF-1,2,3,4,6,7,8				0,1		0,01
HeptaCDF 1,2,3,4,7,8,9						0,01
OctaCDF			0,001			0,001

Table 2: NATO and new WHO Toxic Equivalency Factors (NATO/CCMS, 1988; WHO ECEH/IPCS, 1998):

Congener	NATO	WHO *
Dibenzo-p-dioxins		
2,3,7,8-TCDD	1,0	1.0
1,2,3,7,8-PeCDD	0,5	**1,0**
1,2,3,4,7,8-HxCDD	0,1	0,1
1,2,3,6,7,8-HxCDD	0,1	0,1
1,2,3,7,8,9-HxCDD	0,1	0,1
1,2,3,4,6,7,8-HpCDD	0,01	0,01
OCDD	0,001	**0,0001**
Dibenzofurans		
2,3,7,8-TCDF	0,1	0,1
2,3,4,7,8-PeCDF	0,5	0,5
1,2,3,7,8-PeCDF	0,05	0,05
1,2,3,4,7,8-HxCDF	0,1	0,1
1,2,3,6,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF		0,1
2,3,4,6,7,8-HxCDF	0,1	0,1
1,2,3,4,6,7,8-HpCDF	0,01	0,01
1,2,3,4,7,8,9-HpCDF	0,01	0,01
OCDF	0,001	**0,0001**
Non-ortho PCBs		
PCB 81 (Tetrachlorobiphenyl-3,4,4',5)		0,0001
PCB 77 (Tetrachlorobiphenyl-3,3',4,4')		0,0001
PCB 126 (Pentachlorobiphenyl-3,3',4,4',5)		0,1
PCB 169 (Hexachlorobiphenyl-3,3',4,4',5,5')		0,01
Mono-ortho PCBs		
PCB 105 (Pentachlorobiphnenyl-2,3,3',4,4')		0,0001
PCB 114 (Pentachlorobiphenyl-2,3,4,4',5)		0,0005
PCB 118 (Pentachlorobiphenyl-2,3',4,4'5)		0,0001
PCB 123 (Pentachlorobiphenyl-2',3,4,4',5)		0,0001
PCB 156 (Hexachlorobiphenyl-2,3,3',4,4',5)		0,0005
PCB 157 (Hexachlorobiphenyl-2,3,3',4,4',5')		0,0005
PCB 167 (Hexachlorobiphenyl-2,3',4,4',5,5')		0,00001
PCB 189 (Heptachlorobiphenyl-2,3,3',4,4',5,5')		0,0001

1.6 Relevant Standard methods

The following table gives an overview of the currently available standards and method recommendations published by national or international standardization bodies. There is a great number of scientific literature. In the field of sample cleanup a variety of procedures are described, whereas in the field of GC/MS measurement the methods used are very similar. Apparently it makes no sense to list all those literature in detail, because they already have been incorporated in the standards listed in Table 3.

Table 3: Overview of relevant Standard Methods

Method	Analyte	Matrix	Origin
EN 1948 – 2,3	PCDD/F	Emission	EU
EPA Method 23	PCDD/F	Emission	USA
CARB 428	PCDD/F PCB by groups mono-deca CB	Emission	USA
VDI 3498	PCDD/F	Ambient Air	D
VDI 3499	PCDD/F	Emission	D
JIS K 0311	PCDD/F coplanar PCBs	Emission	Japan
EPA Method T0 9A	PCDD/F	Ambient Air	USA
VDI 3498	PCDD/F	Ambient Air	D
EPA Method 1613	PCDD/F	Soil, water, ash, waste, chemical products, food, feeds, biota and other matrices	USA
EPA Method 8280	PCDD/F	Soil, water, ash, waste, chemical product, distillation residue, fuels, sludge	USA
EPA Method 8290	PCDD/F	Soil, water, ash, waste, chemical product, distillation residue, fuels, sludge, biota	USA
EPS 1/RM/19	PCDD/F	Paper industry products	Canada
EPA Method 1668	Coplanar PCBs	Soil, water, sludge, sediment, biota and other samples	USA
Klärschlammverordnung	PCDD/F	sludge	D,A
Luftreinhalteverordnung für Kesselanlagen, 1989, BGBl, 134/1990	PCDD/F	Emissions	A
ISO/DIS 18073	PCDD/F	Water	INT
Commission Directive 2002/70/EC	PCDD/F, DL-PCB	Feeding stuffs	EC

2 ANALYTICAL METHOD

Methods for the analysis of PCDD/F are available in the literature since many years on a high quality level. New developments of the last years concern mostly the field of automatization.

Isotope dilution method is state of the art for the analysis of PCDD/F and DL-PCB. For extraction of PCDD/F and DL-PCB an organic solvent e.g. toluene, benzene, hexane in a Soxhlet extractor or pressurized solvent extractor like ASE (Dionex) or PLE (FMS) is widely used. Only a few alternative extraction methods exist like Microwave assisted Soxhlet extraction, but they are of minor relevancy. The crucial point is the clean up of the extracts, which must be done very carefully to get high recovery rates and a clean sample solution for the measurement.

Due to a lack of standard methods, laboratories developed their own combinations of effective cleanup steps. Therefore this horizontal standard has to care about this situation and should allow the use of those methods under concern of the quality requirements which will be given in the horizontal standard.

This approach will be verified by international intercalibration studies of PCDD/F and DL-PCB in soil, sediment and sludge samples which were organised by Bert VanBavel, University of Örebro, annually during the last ten years. The results reported by up to 70 laboratories world-wide show a relative standard deviation of less than 25% for soil and sediment samples, after the elimination of outliers. No particular analytical method was stipulated by the organizers of these studies, which means that especially in the field of sample clean up a wide range of different methods were used. Nevertheless a sufficient standard deviation of 25% could be achieved.

As a result it seems to be reasonable for the Horizontal PCDD/F and DL-PCB Standard Method to thoroughly define quality requirements for analysis, without stipulating of a single analytical method. For the ease of use of the future standard a comprehensive annex with analytical methods, which fulfil those requirements, should be added. These methods should serve as not binding recommendations.

This approach is equivalent to the structure of the existing standard EN-1948 (PCDD/F in emission samples).

2.1 Analytical method

A comprehensive standard must cover the following analytical steps:

- Pre-treatment and Subsampling

  A pre-treatment step is necessary to get dry and homogenous samples for the following extraction step. Therefore drying, sieving and/or grinding have to be carried out, with care and attention not to change the levels or the composition of PCDD/F and DL-PCB. Appropriate methods are described in ISO/DIS 11464, ISO/DIS 14507 and ISO/DIS 16720.

- Sample amount

  Typical sample amounts for soil, sludge and bio waste are 5 g to 50 g depending on expected concentration of contamination.

- Spiking

Isotope dilution method is the state of the art for the analysis of PCDD/F and DL-PCB. The samples have to be spiked with isotope (^{13}C) labelled standards before extraction. For PCDD/F the spiking standard has to contend all 17 2,3,7,8-chlorinated congeners, for the DL-PCB all 12 congeners which are included into the TEF-Scheme of WHO (1998). All standard substances, labelled and unlabelled, are commercially available at affordable prices.

- Extraction

  For extraction of PCDD/F and DL-PCB from soil, sludge or bio waste the most widely used method is Soxhlet extraction with an organic solvent e.g. toluene, hexane, cyclohexane. Newer extraction techniques, which are less time and solvent consuming, like pressurized solvent extraction, show comparable results. In general which ever extraction method will be used it has to be shown that the extraction is exhaustive.

- Clean up

  Many different methods for clean up of soil, sludge and bio waste samples are published in the literature. All of these methods are combinations of different kinds of liquid column chromatography techniques to remove interfering matrix components. There are manually methods as well as semi or fully automated methods described. The horizontal standard has to define the minimum requirements for these cleanup steps, which are basically the recovery rates of the labelled substances. Examples of proven techniques for choice should be given in an annex of the standard method, equal to the annexes in EN 1948.

- Analytical Measurement

  As isotope dilution method is mandatory for sufficient analytical quality, the use of GC/MS is the only possibility for detection. The use of GC/HRMS is highly recommended, due to highest possible selectivity and sensitivity. This GC/HRMS can be considered as “Gold Standard” for confirmatory analysis of PCDD/F and DL-PCB. At the moment it is not possible to separate all 17 2,3,7,8-PCDD/F congeners in one single GC run, due to the lack of an appropriate GC column. Therefore it is necessary to do the GC/MS measurement twice, on a polar and on a non-polar phase. Looking at the results of intercalibration studies, it seems that for the DL-PCB a single measurement on a non-polar column is sufficient.

Table 4: Overview of relevant methods for cleanup and quantitative analysis

Matrix	Compounds	Extraction	Clean Up	Method of Detection	Reference
emission	PCDD/F	Soxhlet / Toluene	- gel permeation - multi layer column - active carbon column - alumina column	GC/HRMS	EN 1948-2,3
emission	PCDD/F	Soxhlet / Toluene	- silica gel - basic alumina column - carbon/celite column	GC/HRMS	EPA Method 23
emission	PCDD/F PCB by groups mono-deca CB	Soxhlet / Benzene Soxhlet / Toluene	- silica gel column - silica gel+alumina column - carbopak/celite columns	GC/LRMS GC/HRMS	CARB 428
emission	PCDD/F	Soxhlet / Toluene	- silica gel/alumina column - multi layer column	GC/MS	VDI 3499
emission	PCDD/F coplanar PCBs	Soxhlet / Toluene	- multi layer silica gel column - carbon/silica gel column	GC/HRMS	JIS K 0311
ambient air	PCDD/F, PBDD/F, PBCDD/F	Soxhlet / Benzene Soxhlet / Toluene	- multi layer column - active carbon column - alumina column	GC/HRMS	EPA Compendium Method TO 9A
ambient air	PCDD/F	Soxhlet / Toluene	- multi layer column - alumina column - HPLC	GC/HRMS	VDI 3498
water	PCDD/F	Soxhlet / Toluene	- gel permeation - multi layer column - active carbon column - alumina column - silica column - florisil column - HPLC - $AgNO_3$/silica column	GC/HRMS	ISO/DIS 18073

Table 5: Overview of relevant methods for cleanup and quantitative analysis (continuation of Table 4)

Matrix	Compounds	Extraction	Clean Up	Method of Detection	Reference
water soil sediment sludge tissue	PCDD/F	Not described	- gel permeation - multi layer column - active carbon column - alumina column - solid phase C18	GC/HRMS	EPA 1613 Revision B
water, soil, fly ash, chemical waste, fuel oil, dge	PCDD/F	Dichloromethane Soxhlet / Toluene	- acid-base column - silica gel column - alumina column - carbon column	HRGC/LRMS	EPA Method 8280
soil, sediment, fly ash, paper pulp, water, fuel oil, still bottom, fish, human adipose tissues	PCDD/F	Soxhlet / Toluene Dichloromethane Dean-Stark/Toluene Soxhlet/Hexane-Dichloromethane	- acid-base column - silica gel column - alumina column - carbon column	HRGC/HRMS	EPA Method 8290
water, soil, sediment, sludge, tissue, others	PCB	Dichloromethane Dean-Stark/Toluene Soxhlet/Hexane-Dichloromethane	- acid-base column - gel permeation - silica gel column - florisil column - carbon column	HRGC/HRMS	EPA Method 1668 (isotope dilution)
sewage sludge	PCDD/F	Soxhlet / Toluene	- alumina column - mixed column - X3 bio-beads column	GC/MS	Klärschlammverordnung (A)
feeding stuffs	PCDD/F, DL-PCB	Not described	Not described	GC/HRMS	Commission Directive 2002/70/EC
soil	PCDD/F	Soxhlet / Toluene	- metallic mercury - multi layer column - active carbon column	GC/LRMS GC/HRMS	SAEFL Guidelines

			- alumina column		

2.2 Quality Assurance

The planned approach of the standard is to prescribe minimum quality requirements and to give methods which proof these requirements as examples. Therefore the quality criteria for the analytical method are the most important point of the standard.

The necessary quality requirements are:

- Number (which congeners) and amount of isotope labelled standards
- Minimum and maximum recovery rate of isotope labelled standards
- Minimum signal to noise level of isotope labelled standards
- Limits for deviation from theoretical isotope ratio
- Limits for deviation of retention times
- Chromatographic separation efficiency
- How to calculate the detection limit
- Minimum detection limit
- Trueness, accuracy

Quality requirements already published in scientific literature, national regulations and national and international standards:

The relative standard deviations of international intercalibration studies are below 25% for soil and sediment samples (B. VanBavel, 2003).

The European Commission defines quality requirements for PCDD/F and DL-PCB analysis in feeding stuffs as following: trueness ± 20%, accuracy better than 15%, recovery limits are between 60% and 120% (2002/70/EC).

In EN 1948 there are quality requirements for storage (<4°C, darkness) and clean up (recovery rates between 50% and 130% for Tetrachlorinated-congeners) defined. The detection limit has to be calculated using the Signal to Noise ratio of 3:1 (EN 1948, 1997).

In the guidelines of the Swiss Agency for the Environment, Forests and Landscape (SAEFL) the limits for recovery has to be between 50% and 115%, accuracy 10-15 %, reproducibility 15-25 %. For intercalibration studies deviations for standard solutions up to 10% and deviations for sample extracts up to 20% are acceptable (SAEFL, 2001).

Table 6: Overview of relevant provisions for Quality Assurance

Matrix	Compounds	% recovery	Calculation of Detection Limit	Scope	Reference
emission	PCDD/F	50 – 130 (4-6) 40 – 130 (7-8)	Signal to Noise 3/1	Control of 0.1 ng/m³	EN 1948-2,3
emission	PCDD/F	70 - 130			EPA Method 23
emission	PCDD/F PCB by groups mono-deca CB	60 – 140	Not defined	ng – pg/m^3	CARB 428
emission	PCDD/F	currently not available	Not defined	<0,1 I-TEQ/m^3 >0,1 I-TEQ/m^3	VDI 3499
emission	PCDD/F coplanar PCBs	currently not available	Not defined	<0,1 I-TEQ/m^3	JIS K 0311
Ambient air	PCDD/F, PBDD/F, PBCDD/F	50 - 120	Not defined	Tetra-HxCDD/F: 0,02 – 0,15 pg/m³ Hp-OCDD/F 0,05 - 0,25 pg/m³	EPA Compendium Method TO 9A
Ambient Air	PCDD/F	50 - 130	Signal to Noise 3/1	MDL 0,5 – 3 fg/m³	VDI 3498
water	PCDD/F	50 – 130 (4-6) 40 – 130 (7-8)	Signal to Noise 3/1	Detection of low levels (few pg/l) in water samples	ISO/DIS 18073

Table 7: Overview of relevant provisions for Quality Assurance (continuation of Table 6)

Matrix	Compounds	% recovery	Calculation of Detection Limit	Scope	Reference
water soil sediment sludge tissue	PCDD/F	No limits defined	Not defined	Minimum levels TCDD/F 1 ng/kg Pe-HpCDD/F 5ng/kg OCDD/F 10ng/kg	EPA 1613 Revision B
water, soil, fly ash, chemical waste, fuel oil, dye	PCDD/F	currently not available	Not defined	≥ 0,7 ppb(soil, ash) ≥ 7 ppt (aequous) ≥ 7 ppb (chem.waste)	EPA Method 8280
soil, sediment, fly ash, paper pulp, water, fuel oil, still bottom, fish, human adipose tissues	PCDD/F	40 – 135	Not defined	≤ 10 x MCLs (method calibration limits)	EPA Method 8290
water, soil, sediment, sludge, tissue, others	PCB	21 – 197	Not defined	MDL 40 pg/L (PCB 126)	EPA Method 1668 (isotope dilution)
sewage sludge	PCDD/F	>70	Not defined	ng/kg	Klärschlammverordnung (A)
feeding stuffs	PCDD/F, DL-PCB	60 – 120	No defined	Control of different challenges for feeding stuffs	Commission Directive 2002/70/EC
soil	PCDD/F	50 - 115	MDL 50 fg/µl	Method range 50 fg/µl to 5 ng/µl	SAEFL Guidelines

3 CRITICAL EVALUATION

Soil, sludge and to an even greater extend bio-waste are very heterogeneous matrices, therefore initial sample pre-treatment like drying, grinding sieving has to be carried out with care. Although various methods are available for this purpose like ISO/DIS 11464, ISO/DIS 14507 and ISO/DIS 16720 it may be necessary to give additional provisions, e.g. for sludge drying or bio-waste homogenisation in the future horizontal standard.

The future standard should define a basic quality assurance concept, covering the various analytical methods used and their continuous modification. The quality assurance concept has to comprise all steps of the sample pre-treatment, extraction, clean-up separation, identification, quantification and reporting,

There already exist various validated analytical methods, described in detail in the scientific literature, and international standards for some matrices as well. These methods are at least partly applicable to soil, sludge and bio-waste.

These findings make it clear, that there is no need for a completely new approach for the future standard, but the roadmap to the future horizontal standard is to compile the applicable parts of those methods with respect to the specific needs of soil, sludge and bio-waste, and to find a consensus on quality criteria.

Another conclusion which can be drawn from scientific literature is that the analytical pathways for PCDD/F and DL-PCB are nearly the same. Therefore also analytical provisions for the determination of DL-PCB, should be included in the future standard. This will lead to a cost effective analytical method for both groups of substances.

For the time being it is scientific consensus that for confirmatory analysis of PCDD/F in all matrices only HRGC/HRMS can meet the basic requirements for high sensitivity, high selectivity and high accuracy. Nevertheless the future standard should also include provisions for screening methods which can comprise bio assays and GC/MS methods as well.

4 REFERENCES

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5 ABBREVIATIONS

PCDD	Polychlorinated Dibenzo-p-dioxins
PCDF	Polychlorinated Dibenzofurans
PCDD/F	Polychlorinated Dibenzo-p-dioxins and Dibenzofurans
PBDD/F	Polybrominated Dibenzo-p-dioxins and Dibenzofurans
PBCDD/F	mixed brominated and chlorinated Dibenzo-p-dioxins and Dibenzofurans
TCDD/F	Tetrachlorodibenzo-p-dioxin and Dibenzofuran
PeCDD/F	Pentachlorodibenzo-p-dioxin and Dibenzofuran
HxCDD/F	Hexachlorodibenzo-p-dioxin and Dibenzofuran
HpCDD/F	Heptachlorodibenzo-p-dioxin and Dibenzofuran
OCDD/F	Octachlorodibenzo-p-dioxin and Dibenzofuran
DL-PCB	dioxinlike Polychlorinatedbiphenyls
TEF	Toxic Equivalency Factor
QA	Quality Assurance
LRMS	Low Resolution Mass-Spectrometry
HRMS	High Resolution Mass-Spectrometry
MDL	Method Detection Limit
ASE	Accelerated Solvent Extraction (Product of DIONEX)
PLE	Pressurized Liquid Extraction (Product of FMS)
WHO	World Health Organisation
TEF	Toxic Equivalency Factor
TEQ	Toxic Equivalent
MeCl	Methylenechloride

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