

# **Dioxins**



**OSPAR Commission**  
2007 update

The Convention for the Protection of the Marine Environment of the North-East Atlantic (the “OSPAR Convention”) was opened for signature at the Ministerial Meeting of the former Oslo and Paris Commissions in Paris on 22 September 1992. The Convention entered into force on 25 March 1998. It has been ratified by Belgium, Denmark, Finland, France, Germany, Iceland, Ireland, Luxembourg, Netherlands, Norway, Portugal, Sweden, Switzerland and the United Kingdom and approved by the European Community and Spain.

*La Convention pour la protection du milieu marin de l'Atlantique du Nord-Est, dite Convention OSPAR, a été ouverte à la signature à la réunion ministérielle des anciennes Commissions d'Oslo et de Paris, à Paris le 22 septembre 1992. La Convention est entrée en vigueur le 25 mars 1998. La Convention a été ratifiée par l'Allemagne, la Belgique, le Danemark, la Finlande, la France, l'Irlande, l'Islande, le Luxembourg, la Norvège, les Pays-Bas, le Portugal, le Royaume-Uni de Grande Bretagne et d'Irlande du Nord, la Suède et la Suisse et approuvée par la Communauté européenne et l'Espagne.*

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## Executive Summary/Récapitulatif

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are two groups of tricyclic, chlorine-substituted, organic compounds. The number of chlorine substituents on the benzene rings may range from one to eight, which means 75 theoretical possible PCDDs and 135 possible PCDFs congeners, identified in general by the name "dioxins". Dioxins are non-polar, lipophilic and persistent organic pollutants (POPs), which are able to biomagnify and bioconcentrate in the food web and cause a whole spectrum of potentially serious health problems.

*Les polychlorodibenzo-*p*-dioxines (PCDD) et les polychlorodibenzofuranes (PCDF) sont deux groupes de composés organiques tricycliques, dont le chlore est substitué. Le nombre de substitués du chlore sur les anneaux de benzène peut aller de un à huit, ce qui signifie qu'il peut théoriquement exister 75 congénères des PCDD et 135 congénères des PCDF, lesquels sont d'une manière générale qualifiés de « dioxines ». Les dioxines sont des polluants organiques persistants (POP), non polaires et lipophiles, capable de se biomagnifier et de se bioconcentrer dans la chaîne alimentaire et de provoquer toute une série de problèmes de santé potentiellement graves.*

Dioxins are mainly formed as unintentional by-products in heating and combustion processes involving organic matter, chlorine compounds and a catalyst, e.g. copper, or in the production of certain chlorinated chemicals and pulp bleaching. Formation of trace concentrations of dioxins may take place in any fire or combustion process based on natural or man-made organic materials. The presence of chlorinated organic compounds, such as chlorophenols, chlorobenzenes, chlorodiphenyl ethers and polychlorinated biphenyls (PCBs) may accelerate the dioxin formation.

*Pour l'essentiel, les dioxines sont des sous-produits involontaires des processus de chauffage et de combustion de la matière organique, des composés chlorés et d'un catalyseur, par exemple le cuivre, ou de la fabrication de certains produits chimiques chlorés et du blanchiment de la pâte à papier. Des dioxines à des teneurs en traces peuvent se former dans tout feu ou toute combustion de matières organiques naturelles ou de synthèse. La présence de composés organiques chlorés, tels que les chlorophénols, les chlorobenzènes, les éthers chlorodiphényles et les polychlorobiphényles (PCB) peut accélérer la formation des dioxines.*

Because dioxins are found in the environment as various different congener mixtures, a variety of toxicity equivalency systems have been developed in order to simplify the assessments of impacts and to compare results and trends. These systems express the toxicity of each dioxin congener relative to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (e.g. toxicity equivalency factors (TEF), TCDD equivalents (TEQ), etc.). Remark the system of toxicity makes no difference between short term and long term toxicity. Due to the extremely low water solubility, very low concentrations of dioxins are found in the water phase, but an accumulation in sediments is detected. Dioxin levels in fish and aquatic organisms vary according to the species, size and area caught. Herrings, salmon and other fishes with high lipid content have high dioxin levels expressed on fresh weight basis and levels increase with size/age. Marine mammals such as seals have the highest dioxin contamination and in the polluted area as the Baltic Sea levels may be 30 times higher than in seals from the Atlantic.

*Du fait de la présence de dioxines sous la forme de divers mélanges de congénères, toute une série de systèmes d'équivalence de toxicité a été mise au point pour simplifier l'évaluation des impacts et pour comparer les résultats et les tendances. Ces systèmes permettent d'exprimer la toxicité de chacun des congénères des dioxines par rapport à la 2,3,7,8-tétrachlorodibenzo-*p*-dioxine (p.ex. les coefficients d'équivalence de toxicité (TEF), les équivalents TCDD (TEQ), etc.). Remarque que le système des coefficients d'équivalence de toxicité ne compte pas avec toxicité de court ou long terme. En raison de leur très faible solubilité dans l'eau, on trouve des dioxines à de très faibles teneurs dans la phase aqueuse ; en revanche, on en observe l'accumulation dans les sédiments. Les teneurs en dioxines chez le poisson et dans les organismes aquatiques varient en fonction de l'espèce et de la zone.*

The main existing international agreements on dioxins are: the UN ECE protocol on POPs requiring mandatory control measures and establishing emission limit values, and the UNEP POPs Convention requiring measures for reducing or preventing releases of dioxins to the environment. EC Directives on integrated pollution prevention and control, on the incineration of wastes and the Seveso Directives are also relevant. A communication on an EU strategy on PCBs, dioxins and furans was adopted by the European Commission in 2001 identifying a number of gaps in the achievement of the objectives set up in EU legislation, the fifth Environment Action Programme, and identifying gaps in knowledge. The communication implied an integrated and systematic approach to reduce the presence of PCBs, furans and dioxins in the

environment and the necessity to identify short- to medium term and long-term actions, in particular with regard to establishing maximum limits in food and fodder.

*Les principaux accords internationaux portant sur les dioxines sont le Protocole sur les POP, de la Commission économique des Nations Unies pour l'Europe, qui prévoit des mesures de lutte obligatoires et qui fixe des plafonds d'émission, et la Convention du PNUE sur les POP, qui impose des mesures de réduction ou de prévention des émissions de dioxines dans l'environnement. Les Directives communautaires européennes, visant la prévention de et la lutte intégrées contre la pollution ainsi que l'incinération des déchets, et enfin les directives dites de Seveso sont également pertinentes. Une communication relative à une stratégie communautaire européenne visant les PCB, les dioxines et les furanes a été adoptée par la Commission européenne en 2001 ; elle définit un certain nombre de lacunes dans la réalisation des objectifs fixés par la législation de l'Union européenne, le cinquième Programme d'action pour l'environnement, ainsi que les lacunes des connaissances. La communication implique une approche intégrée et systématique afin de réduire les teneurs en PCB, en furanes et en dioxines dans l'environnement, ainsi que la nécessité de fixer des mesures à court, moyen et long terme, en particulier de fixer des plafonds dans les produits alimentaires et les aliments pour animaux.*

The action recommended is: to review the implementation of the communication on a EU strategy on PCBs, dioxins and furans; to review what action might be appropriate in such areas and sources not covered by integrated pollution prevention and control systems in particular with regard to contaminated waste and the promotion of substitution of materials, products and processes leading to the unintentional formation of dioxins and furans; and to ask other relevant international forums to take account of this background document.

*Les mesures recommandées sont les suivantes : réexaminer la mise en oeuvre de la communication relative à une stratégie communautaire européenne visant les PCB, les dioxines et les furanes ; considérer quelles mesures s'imposeraient dans les domaines et pour les sources non couvertes par les systèmes de prévention de et de lutte intégrées contre la pollution, en particulier en ce qui concerne les déchets contaminés, ainsi que la promotion de la substitution des matières, produits et procédés aboutissant à la formation involontaire des dioxines et des furanes ; et enfin demander aux autres instances internationales compétentes de prendre en considération le présent document de fond.*

A monitoring strategy for dioxins is attached to this background document.

*Une stratégie de surveillance sur les dioxines est jointe à ce document de fond.*

## Note

Information on emissions of dioxins has been compiled based through information submitted by Contracting Parties. As techniques and effort to assess emissions have varied over time and were developed independently, this has resulted in various degree of consistency and comparability. Nevertheless, the data presented in the Background Document allow the formulation of reduction and monitoring strategies in the OSPAR regime.

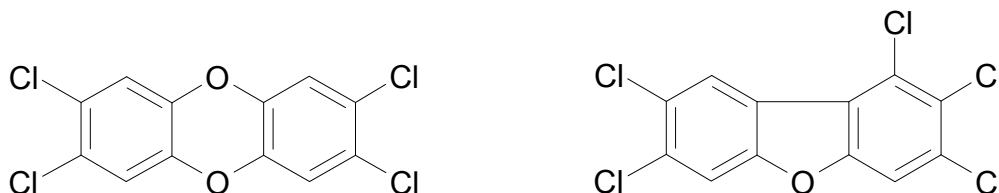
Emission data for OSPAR Contracting Parties have been compiled and made available through the Convention on Long Range Transboundary Air Pollution as part of its EMEP programme. Under the Stockholm Convention new reporting has also started.

# 1. Identification of all Sources of Chlorinated Dibenzo-*p*-dioxins and Chlorinated Dibenzofurans and their Pathways to the Marine Environment

## 1.1 Introduction to the chemical family

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are two groups of tricyclic, chlorine-substituted, organic compounds. The number of chlorine substituents on the benzene rings may range from one to eight, which means 75 theoretical possible PCDD congeners<sup>1</sup> and 135 possible PCDF congeners. These 210 “family members” (PCDD + PCDF, PCDD/F) are often identified by the name: “dioxins”. Each group of isomers has an abbreviated name such as TCDD, TeCDD, TetraCDD or Cl<sub>4</sub>CDD for the most famous and hazardous family member: 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin, better known as the Seveso-dioxin. Sources of coplanar PCBs with dioxin-like toxicity are not included in this report.

The “dioxin” molecules are almost all planar. The chemical structure formulas of two examples of congeners are shown in Figure 1.1:



**Figure 1.1: Examples of dioxin congeners: 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin and 1,2,3,7,8-Pentachlorodibenzofuran.**

The analogous polybrominated dibenzo-*p*-dioxins (PBDDs), polybrominated dibenzofurans (PBDFs) and polychlorinated dibenzothiophenes (PCDTs) have quite similar properties, as the normal “dioxins” but are less abundant.

Dioxins are non-polar, lipophilic and persistent organic pollutants (POPs), which bioaccumulate in the food chain. Congeners with chlorine substitution in the 2,3,7,8-positions are most persistent, bioaccumulative and toxic.

The solubility in water is extremely low and decreases with increasing level of chlorination. For instance, the solubility of 2,3,7,8-TCDD is in the order of 20 ng/l, while the solubility of 1,2,3,4,6,7,8,9-octachlorodibenzo-*p*-dioxin (OCDD) is about three orders of magnitude lower.

The octanol-water partition coefficient (expressed as log  $K_{ow}$ ) increases with chlorine content and ranges from 6.80 for 2,3,7,8-TCDD to 8.20 for OCDD. These values are among the highest reported for environmental contaminants and indicate that dioxins will have a high affinity for organic matter, fats and oils.

<sup>1</sup> Includes both “isomers” (different *positions* of a certain number of chlorine substituents) and “homologues” (different *number* of chlorine substituents). For example, all HxCDDs are isomers, whereas, HxCDDs + HpCDDs are homologues.

Dioxins are very stable chemicals. Generally, dioxins are not degraded by microorganisms, strong acids and bases, heat or light, and remain stable at temperatures below 750°C. The biodegradation is slowest for the high-chlorinated congeners.

## 1.2 Chemical analysis for dioxins

Very low (parts-per-trillion, ppt, pg/g) levels of dioxin occur widespread in the environment; they represent mixtures of various congeners in different concentrations. A congener-specific determination of such low levels of dioxins requires time, resources, experienced chemists and the most advanced instruments. The resulting congener pattern will differ between sources and is as characteristic as a fingerprint, and it can possibly be used for indicating the origin of the dioxin contamination. However, it has to be taken in account that only slight differences in the congener pattern of environmental samples, such as deposition samples, can be noticed, due to the variable degradation rate of the different congeners. "In addition to this, it is often difficult to link the pattern observed in environmental samples and the source, because of the differential pathway of individual congeners (degradation, bioaccumulation)."

Nowadays, the chemical determination of dioxins is based on high-resolution gas chromatography combined with high-resolution mass spectrometry (HRGC-HRMS). The analysis is preceded by a time-consuming and very specialised clean up of samples. HRMS is a very expensive technique that is not accessible to the majority of laboratories. As a consequence there is a shortage in laboratories capable of analysing dioxins. This is of special importance, when the large scale monitoring of these compounds is considered. An overview of the analytical technique was presented at a UNEP POP Workshop in Geneva, 24-27 March 2003 (1).

There are, nonetheless, a number of recent and attractive alternatives for HRMS. Comprehensive GC (GCxGC) is a prime example of a chemical method. It is a more advanced form of the hart-cut two-dimensional chromatography, a technique that has proven its value, amongst other things, for the determination of PCBs. Because of the efficient refocusing of peaks in the modulator of a GCxGC, a ten to twenty-fold increase of the sensitivity can be obtained (2). This makes this technique an attractive alternative for the expensive HRMS analysis. However, the technique is still in full development and therefore ill-suited for a large-scale application.

Low resolution MS/MS with an ion trap is another alternative worthwhile mentioning, as is low-resolution mass spectrometry with negative chemical ionisation (NCI-LRMS) (3). Here also, the analysis is preceded by an extensive and, in certain cases, a very selective sample clean up. For instance, a method with pyrenyl-silica columns for the determination of planar PCB's that allows the simultaneous fractionation of dioxins (4). A drawback of NCI-MS is the lower sensitivity for molecules with 4 chlorine atoms or less. However, modern injection techniques such as large volume injection (LVI) can provide an answer to this.

In the last years, mass spectrometry based on ion-trap analysers (ITMS) has become an interesting alternative at low cost to the high-resolution mass spectrometry (HRMS) for the analysis of organic contaminants in food and environmental samples. The popularity of GC-ITMS is based on a favourable combination of excellent sensitivity in full-scan mode and high selectivity using tandem mass spectrometry (MS/MS). The ITMS system is a three-dimensional quadrupole mass analysis device. The operation of the ITMS differs from other MS techniques, because the ions are formed, stored in an electric field, and then ejected according to their mass/charge ratio, to the detector. Because it is an ion storage device, the ITMS is inherently more sensitive than pass-through mass filters such as quadrupole instruments. In addition, the ability of ITMS to manipulate ions in time during storage for ion dissociation or reaction allows obtaining a high selectivity in the analysis of complex matrices. The use of ion trap tandem mass spectrometry has given a new dimension to the problems involved in the analysis of polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), and biphenyls (PCBs). It can resolve the analysis of several PCB isomer pairs and minimise the matrix interference. Besides high-resolution MS, ion-trap tandem mass spectrometry has been applied for the analysis of PCDDs and PCDFs in some environmental samples, but further studies related with the applicability and validation of this technique to the analysis of these compounds in environmental, food and feed samples should be performed (5).

Finally, LRMS is a common appearance in most environmental laboratories today. It is, in any case, more affordable than HRMS. Methods for dioxin determination that are therefore based on both MS/MS and NCI-MS are open to a much larger number of laboratories. This is of particular importance, if large-scale monitoring programmes are envisioned.



### 1.3 Bioassays for monitoring of dioxins

The dioxin receptor CALUX<sup>®2</sup> and HRGS<sup>3</sup> cell-based *in vitro* bioassay methods developed for analysis dioxin-like substances are much cheaper and faster than the conventional chemical HRGC-MS<sup>4</sup> methods. These systems incorporate a firefly gene into a cultured mouse cell line or a cultured human cell line, respectively. When exposed to dioxin-like compounds, these systems produce the enzyme luciferase, which react with luciferin and emits light of a characteristic wavelength with intensity proportional with the dioxin concentration. These methods also apply different extraction and clean-up procedures.

In June 2002 the U.S. EPA did report a comparison exercise between CALUX, HRGS and HRGC-MS demonstrating that neither of the bioassay methods produced results that were identical to the chemical method (6). Both bioassays tended to produce results higher than the chemical method by measuring all chemicals able to bind to the dioxin receptor. It was concluded that the methods could be useful as screening methods associated with a specific action level, because if the bioassay results are below the action level, it is most likely that results by the chemical method also would have been below. Good correlations were usually observed at validation and interpretation of the CALUX bioassay results obtained for marine biological matrices compared with results obtained from use of advanced chemical methods as discussed by Belgian and Dutch scientists (7,8). An intra- and interlaboratory study of using CALUX for analysis of dioxins and dioxin-like chemicals in dredged sediments also concluded that the tool was accurate and reliable for monitoring of coastal sediments (9).

### 1.4 Toxicity and evaluation criteria for the marine environment

The toxicological effects of dioxins and furans have mostly been studied in mammalian systems. PCDDs and PCDFs cause a whole spectrum of potentially serious health problems that can occur if sufficient residue is present. The health effects, however, are species-, congener-, and gender-dependent and are probably the result of differences in body fat composition of species, or of differences in metabolism (10,11). Nevertheless, although the amount of chemical required to produce a toxic response is different, once toxicosis is induced, the effects observed appear to be very similar.

The type of exposure (acute vs. chronic) and the amount of exposure are also important determinants of the ultimate toxic effects of PCDD and PCDF exposure. In test animals, exposure to PCDD and PCDF congeners has caused liver enlargement, liver lesions, immunotoxicity, a wasting syndrome, thymic and spleen atrophy, tissue specific hypo- and hyperplastic responses, carcinogenesis, and endocrine disruption, (12-16). Toxic effects of the human skin include chloracne, hypertrichosis, and hyperpigmentation (17, 18). In 1997 2,3,7,8-TCDD became classified as a human carcinogen by IARC (19). On 23 November 2001, a U.S. Federal Court judged TCDD as a known human carcinogen (20).

Binding to and activating the aryl hydrocarbon receptor (AhR) is the initial step in the biological and toxicological effects of dioxins (21). While this is the initial step, it is certainly not the sole determinant in the toxicity of these chemicals. The exact role of the AhR is however unclear, but research links it to an important function in developmental and homeostatic functions. This property of PCDDs and PCDFs allowed an internationally accepted approach to the estimation of risks associated to the exposure of these compounds.

### 1.5 The toxicity equivalency systems

Dioxins in the environment occur as various, different congener mixtures. In order to simplify a risk assessment of the impacts of a total congener mixture, various systems of *toxicity equivalency factors* (TEFs) have been developed, expressing the toxicity of each dioxin congener relative to 2,3,7,8-TCDD (TEF = 1). These systems are mainly based on the potential of binding of the individual congener to the aryl hydrocarbon receptor.

By multiplying the concentration of each congener with the corresponding TEF-value, the *TCDD equivalents* (TEQs) of each congener concentration are obtained. The total of all calculated single TEQs will then result in the TEQ concentration of the sample.

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2 The chemical activated luciferase gene expression procedure that incorporates a firefly gene into a cultured mouse cell line.  
3 The human reporter gene systems that incorporates a firefly gene into a cultured human cell line.  
4 High resolution gas chromatography - mass spectrometry.

It is much easier to oversee and to compare results and trends, when TEQs are used. However, some information is lost on e.g. congener pattern. The scientific relevance of using TEQs to express result is greater for human exposures than for evaluation of pollution sources and emissions. The reason is that the emitted dioxin mixture will change its composition before it reaches the human body, because the different congeners have different degradation and accumulation rates in the environment and food chain.

There are a number of TEF systems, which are not directly comparable. Some of the most important TEF-systems are shown in Table 1.1.

The International System (I-TEF) was until recently the basis for the CEN standard for measurement of dioxin air emissions (EN 1948). Earlier, the Nordic System (N-TEF) was used in the Scandinavian countries. The German System and the USEPA System are also obsolete. However, many data in the literature has been reported in these older or unspecified TEF-systems. It is especially relevant to note that the German System is the only one to include other congeners than 2,3,7,8-substituted congeners. Thus results expressed in these German TEQs will, in general, be much higher than other results. This has to be taken into account when evaluating trends. The more recent system from WHO is not very different from the International System, except for the assessment of pentachloro- and octachloro-congeners, and the inclusion of TEFs for dioxin-like coplanar PCBs. In the beginning, this system was mainly used in connection with food and fodder and human risk assessment but nowadays it is the normal choice in all instances, although PCB TEFs are not always taken into account.

A WHO expert meeting held in Geneva June 2005 has revised the TEF values for dioxin and PCB based on a database covering all relevant studies since 1997 (22). The new values:

- OCDD and OCDF increased from 0.0001 to 0.0003
- 23478-PeCDF decreased from 0.5 to 0.3
- Mono-*ortho*-PCBs now 0.00003 for every congener (earlier: 0.00001-0.0005)

This change will cause a 10-25% decrease in TEQ-content for food matrices.

In 1998, a WHO Expert Group has recommended a tolerable daily intake of 1-4 pg WHO-TEQ/kg body weight (23).

**Table 1.1: Important toxicity equivalency factor systems for dioxins**

Congener	WHO 2005	WHO 1998	International 1989	USEPA 1989	Nordic 1988	German 1985
	WHO-PCDD/F-TEF	WHO-TEF	I-TEF	EPA-TEF	N-TEF	BGA-TEF
2,3,7,8-TCDD	1	1	1	1	1	1
Other TCDDs	0	0	0	0	0	0.01
1,2,3,7,8-PeCDD	1	1	0.5	0.5	0.5	0.1
Other PeCDDs	0	0	0	0	0	0.01
1,2,3,4,7,8-HxCDD	0.1	0.1	0.1	0.04	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1	0.1	0.04	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1	0.1	0.04	0.1	0.1
Other HxCDDs	0	0	0	0	0	0.01
1,2,3,4,6,7,8-HpCDD	0.01	0.01	0.01	0.001	0.01	0.01
Other HpCDDs	0	0	0	0	0	0.001
OCDD	0.0003	0.0001	0.001	0	0.001	0.001
2,3,7,8-TCDF	0.1	0.1	0.1	0.1	0.1	0.1
Other TCDFs	0	0	0	0	0	0.01
1,2,3,7,8-PeCDF	0.05	0.05	0.05	0.1	0.01	0.1
2,3,4,7,8-PeCDF	0.3	0.5	0.5	0.1	0.5	0.1
Other PeCDFs	0	0	0	0	0	0.001
1,2,3,4,7,8-HxCDF	0.1	0.1	0.1	0.01	0.1	0.01
1,2,3,6,7,8-HxCDF	0.1	0.1	0.1	0.01	0.1	0.01
2,3,4,6,7,8-HxCDF	0.1	0.1	0.1	0.01	0.1	0.01
1,2,3,7,8,9-HxCDF	0.1	0.1	0.1	0.01	0.1	0.01
Other HxCDFs	0	0	0	0	0	0.0001
1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01	0.001	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01	0.01	0.001	0.01	0.01
Other HpCDFs	0	0	0	0	0	0.00001
OCDF	0.0003	0.0001	0.001	0	0.001	0

The general formula for the calculation of WHO-TEQs is:

$$TEQ = \sum_i (PCDD_i \cdot TEF_i) + \sum_i (PCDF_i \cdot TEF_i) + \sum_i (PCB_i \cdot TEF_i)$$

Many 10-20 years old dioxin data have been reported as total amounts of PCDD+PCDF without using toxic equivalents. A conversion factor of I-TEQ = 0.015 PCDD+PCDF is often used for rough estimates.

Although the use of TEFs and TEQs is widely accepted, the results should be interpreted carefully. TEQ estimates do not take the bioavailability of a given compound into account and the potential risk can therefore be overestimated (24). Because these compounds are formed as unwanted by-products, they usually are found in mixtures that contain a number of different PCDD and PCDF congeners and other halogenated aromatic hydrocarbons. The TEQ approach assumes only additive effects of all of these compounds, when both synergistic and antagonistic effects have been documented (15,24).

## 1.6 Dioxin formation and destruction processes

Dioxins have no commercial use other than small amounts in analytical standards and as test chemicals. Dioxin congeners can be synthesised by reaction of phenols with chlorobenzenes.

The main sources of dioxins are heating and combustion processes involving organic matter, chlorine compounds and a catalyst, the most efficient being copper. The optimal formation temperatures are between 250 and 500°C, provided oxygen is present. In reality, formation of trace concentration of dioxins may take place in any fire or combustion process based on natural or man-made organic materials, inclusive fossil fuels.

The occurrence of precursors such as chlorophenols, chlorobenzenes, chlorodiphenyl ethers and PCBs may accelerate the dioxin formation. Exposure of such dioxin precursors to UV-light may also lead to photochemical dioxin formation.

Dioxins are also formed under natural conditions during heating processes and during forest- and grass fires. It has recently been discovered that natural sedimentary materials, such as clay and lime, can contain traces of dioxins with a congener pattern different from dioxin formed during combustion. Investigations of cores of sediments or museum samples of soils and vegetation have shown that dioxins were present 150 years ago but the current levels are at least ten-fold higher (25). A more recent investigation of sediment cores from Tokyo Bay shows a trend profile indicating insignificant levels before 1957, maximum levels (30 times) in the early 1980s, which were decreased three-fold in 1992 (26). A similar picture with a decrease in background levels has been found in investigations in Europe and other parts of the world.

Dioxins can be formed as by-products in chemical reactions, e.g. involving chlorophenols or chlorine bleaching agents, and thus may occur as contaminants in chemicals and household products of various kinds. The recent phasing out of chlorine in many processes in many countries has decreased the problem. Attention should also be paid to a number of recycling processes involving metals, glass etc. that may lead to combustion of organic materials present in these products such as paint, plastic and dirt.

Biological formation of dioxins from precursors - at least from chlorophenols - has been observed in composting processes.

Dioxins are likely to be decomposed at very high temperatures (above 800-1000 °C) in power plants and incinerator furnaces, assuming adequate residence time and homogeneous temperature in the combustion chamber; however re-formation of dioxins - secondary formed dioxins - may take place afterwards at lower temperatures in flue gas (27-29).

## 1.7 Overview of pollution sources and congener patterns

Dioxin sources may consist of industrial point sources and diffuse sources from the life cycle of products. In recent years diffuse and secondary dioxin sources have become increasingly important.

Globally, less than 20 countries have made national dioxin inventories and only a few countries have updated their inventories regularly. An overview of all inventories until 1999 has been presented by UNEP (30). In addition, an European Dioxin Inventory has been established as part of a EU research project with reported data of 1993-1995 and subsequently estimated data (31,32). In the European reports the very detailed EMEP/CORINAIR 94 SNAP codes were used to describe the sources. These codes have been developed for European and national reporting on common air emissions. They are sometimes too detailed for reporting the few existing dioxin data, or they lack specific codes for some of the major dioxin sources.

Twelve of the fifteen OSPAR States have published national inventories or have reported such inventories to the European Dioxin Inventory. In the update of the European Dioxin Inventory new national inventories have been presented by France, Poland, Estonia and Latvia. This information has different levels of detail and was collected at different times. Not all inventories have considered all known sources, some examined only industrial sources and some were limited to a small subset of sources. There was no consistent means of handling and presenting data and some data was out of date. This has led to the situation that some of the inventories do not address potentially important sources of PCDD/PCDF, possibly due to insufficient information on a national basis. This could lead to the wrong conclusion that these sources are not significant, and could thus prevent the development of effective controls. Furthermore, only a few inventories address releases to other compartments than to the atmosphere in detail (33-47).

A flow analysis of dioxins for the Tarragona Province only in Spain has been published (48).

Emission inventories might underestimate the polluting capacity of certain types of industries. Belgium has gained a lot of experience in the determination of environmental dioxin and PCB-levels by use of a large

dioxin deposition monitoring network. It appears that for some industrial sectors, only part of the dioxin pollution can be quantified by the measurement of stack emissions. Therefore, in Belgium, deposition measurements are used in a standard way to estimate the environmental dioxin levels, to follow up the impact of sanitation programs and to locate unknown sources.

### 1.7.1 The UNEP tool kit

The UNEP Convention on Persistent Organic Pollutants (POPs) adopted in Stockholm in May 2001 and entered into force 17 May 2004, requires measures for reducing or preventing releases of dioxins to the environment (49). In Annex C to the Convention, the following man-made source categories are mentioned with potential for high formation and release of dioxins:

- Waste incinerators, including co-incineration of municipal, hazardous or medical waste or sewage sludge;
- Cement kiln firing hazardous waste;
- Production of pulp using elemental chlorine, or chemicals generating elemental chlorine, for bleaching;
- Thermal processes in the metallurgical industry (sinter plants in the iron and steel industry and secondary aluminium, copper and zinc production);
- Existing PCDD/PCDF inventories are not satisfactory for the purpose of international reporting and comparison, as they were not compiled in a comparable form.

Existing PCDD/PCDF inventories are not satisfactory for the purpose of international reporting and comparison, as they were not compiled in a comparable form.

In order to enable a reasonable straightforward assembly of national and regional dioxin inventories, which is consistent and comparable, UNEP has developed a standardised methodology (tool kit) for the identification and quantification of dioxin releases in a consistent and resource-effective manner. A new extended Edition 2.1 of the tool kit was published in December 2005 (50).

The first step of the tool is to identify the main source categories and emission endpoints as seen in the screening matrix in Table 1.2:

**Table 1.2: UNEP screening matrix – main source categories**

UNEP No.	UNEP Main Source Categories	Air	Water	Land	Product	Residue
1	Waste Incineration	X				X
2	Ferrous and Non-Ferrous Metal Production	X				X
3	Power Generation and Heating	X		X		X
4	Production of Mineral Products	X				X
5	Transport	X				
6	Uncontrolled Combustion Processes	X	X	X		X
7	Production and use of Chemicals and Consumer Goods	X	X		X	X
8	Miscellaneous	X	X	X	X	X
9	Disposal	X	X	X		X
10	Identification of Potential Hot-Spots	Probably registration only to be followed by site-specific evaluation				

When a national inventory is made, these ten categories have various subcategories, which have to be mapped in more detail in separate tables. For dioxins sources, in general, direct emissions to the air are most important, and every main category has emissions to the atmosphere but not to all the other environmental compartments.

The two main ways of calculating annual air emissions of a source are:

- Using an emission factor (e.g. 1 ng/tonne) multiplied by the annual activity/consumption rate (e.g. 1000 tonnes);
- Using calculated emission fluxes (e.g. 1 ng/hr) multiplied by the number of annual operational hours. The emission flux is calculated by multiplying measured emission concentrations (e.g. pg/Nm<sup>3</sup>) with the flue gas flow rate (Nm<sup>3</sup>/hr).

### 1.7.2 Waste incineration

This UNEP Category 1 includes: municipal solid waste, hazardous waste, medical waste, shredder waste, sewage sludge etc. The UNEP screening matrix with added snap codes and UNEP default emission factors in µg TEQ/tonne for the modern state-of-the-art technology is illustrated in Table 1.3. Details are mentioned in the text and found in the toolkit. In the new version of the Toolkit there is no differentiation/specification of TEQ-system. The values cover PCDD/Fs in WHO, International and Nordic systems.

**Table 1.3: UNEP Category 1: Waste incineration; and ranges of emission factors (µg TEQ/tonne).**

UNEP No.	SNAP Code	Subcategories for waste incineration	Air	Water	Land	Product	Residue
1a	90201	Municipal solid waste	0.5-3500	X			16-500
1b	90202	Hazardous waste	0.75-35000	X			30-9000
1c	90207	Medical waste	1-40000	X			20-920
1d	-	Light-fraction shredder waste	1-1000				150
1e	90205	Sewage sludge	0.4-50	X			0.5-23
1f	-	Waste wood and waste biomass	1-100				0.2-1000
1g	90902	Animal carcasses	5-500				X

"X" means not quantified

Traditionally, incinerations of municipal solid waste, medical/clinical waste and hazardous waste have been considered as some of the most important dioxin sources. The emissions will depend on the composition of the waste (dioxin precursors, chlorine and copper content), the combustion conditions (temperature, oxygen) and the cleaning process of the flue gases (filters, wet scrubbers, cooling). The emissions will mainly be to the atmosphere, and following the use of the more efficient filters pollution will shift to the residues (fly ash). A not to be neglected amount may be emitted with scrubber water depending on the position of the scrubber in the process. The UNEP emission factors for old incinerators without air pollution control are 3500 µg TEQ/tonne municipal waste, 35 000 µg TEQ/tonne hazardous waste and 100 µg TEQ/tonne for waste wood. Recent regulations have considerably reduced dioxin emissions from municipal waste incineration in most OSPAR States as discussed in Chapter 2.

The importance of the chlorine content in waste as well as its chemical form has been discussed before in detail. Higher chlorine content has a potential for the formation of more dioxins; however, the chemical form of chlorine does not always appear to be as important, if the substance concerned is not directly a dioxin precursor. The role of the PVC content in waste for dioxin formation has been controversially discussed, and the results of studies have been conflicting. The World Chlorine Council and a TNO report (51, 52) claim no significant influence, while Greenpeace International and other non governmental organisations are of the opposite opinion. Other studies have shown that an open PVC fire generates and emits considerable amounts of dioxins (53). In a recent Japanese study combustion of newspaper impregnated with NaCl had 50% lower dioxin formation than combustion of newspaper with PVC (54); in another study the chlorine source was unimportant for the formation of chlorinated organic pollutants (55).

The combustion conditions may be more decisive, and very important is also an instant cooling of flue gases to lower than 250°C in order to prevent re-formation of dioxins after the combustion chamber. Last but not least, the design and operation of the cleaning systems before the flue gases leave the stack are most crucial.

Previously clinical waste was incinerated in small and simple installations at hospitals; however, nowadays co-incineration of medical waste with municipal waste is usual. The UNEP emission factor for old incinerators without air pollution control is 40 000 µg TEQ/tonne clinical waste.

Light-fraction shredder waste is mainly reused; there is no available information about dioxin emissions from incineration. The UNEP emission factor for old incinerators without air pollution control measures is 1 000 µg TEQ/tonne light shredder waste.

In general, sewage sludge is used as a fertiliser on agricultural land (see later UNEP Category 9: Disposal). Because sewage sludge may contain traces of dioxins and other pollutants, it is now often incinerated in special plants. Due to sewage sludge containing organic matter and chlorides, this incineration may generate and emit dioxins depending on plant technology applied. Data from Denmark, the Netherlands and the UK indicate air emission factors of 3 - 9 µg I-TEQ/tonnes sludge (dry weight) for newer plants. In older plants emissions can be ten times higher. The UNEP emission factor for old sludge incinerators without air pollution control measures is 50 µg TEQ/tonne dry weight sewage sludge.

Incineration of animal carcasses has become increasingly relevant due to foot-and-mouth and the bovine spongiform encephalopathy (BSE) diseases. The UNEP emission factor for older furnaces is 500 µg TEQ/tonne for animal carcasses.

Incineration of specific industrial waste such as used tyres is not a subcategory in the UNEP toolkit. Waste wood is included, although it will overlap UNEP Category 3: Power generation and heating, where the use of waste wood as 'biofuel' is included.

### **1.7.3 Metal production**

Only recently the importance of ferrous and non-ferrous metal industries has become apparent as dioxin sources. These sources have become relatively more important than other dioxin sources. Beforehand there has been no recognition that there would be sufficient organic matter and chlorine compounds involved in these processes.

It has to be taken in account that a substantial part of dioxin emissions released by the non ferro industry are diffuse emissions. Deposition measurements carried out on a non ferro plant in Belgium (Flanders region) revealed that the dioxin deposition remained high even after the stack emissions were abated. It appeared that the environmental dioxin pollution was related to the storage of fine-grained materials in open air, the dispersion of historical dioxin-loaded dust and the careless handling of risk materials. A profound dust control program and a risk analysis of suspicious materials resulted in a decrease of the dioxin pollution in the surroundings of the non ferro plant.

In Table 1.4 the UNEP screening matrix is shown for Category 2: Ferrous and non-ferrous metal production and default emission factors for modern state-of-the-art technology.

**Table 1.4: UNEP Category 2: Ferrous and non-ferrous metal production; and range of emission factors ( $\mu\text{g TEQ/tonne product}$ )**

UNEP No.	SNAP Code	Metal production subcategories	Air	Water	Land	Product	Residue
2a	30301/40209	Iron ore sintering	0.3-20				0.003
2b	-	Coke production	0.3-3	0.06	X	X	X
2c	40200/30303	Iron and steel production and foundries	0.01-10				0.2-2000
2d	30306/30309	Copper production (with scrap)	0.01-800				300-630
2e	40301/303010	Aluminium production (with scrap)	0.3-150				100-400
2f	30304/30307	Lead production	0.5-80				5
2g	30305/30308	Zinc production (with scrap)	0.3-1000				X
2h	-	Brass and bronze production	0.1-10				125
2i	40304/30323	Magnesium production	3-250	24-9000			0-9000
2j	-	Other non-ferrous metal production	2-100	X			X
2l	-	Shredders	0.2				X
2m	-	Wire reclamation	3.3-5000	(X)	X		X

“X” means not quantified

Iron ore sintering and other sintering processes are major sources together with the production of coke to be used in iron and steel production. Secondary steel production may represent an even more important source, because the scrap may contain residues of other metals, cutting oils and plastic. However, installation of best available techniques means that the dioxin air emission factor can be decreased from around 20  $\mu\text{g TEQ/tonne scrap}$  to <2  $\mu\text{g TEQ/tonne scrap}$ .

Secondary copper production is also an important dioxin source; an emission factor of 1 mg BGA-TEQ/tonne secondary copper has been published (56). The UNEP default factor for old secondary copper smelters is 800  $\mu\text{g TEQ/tonne copper produced}$ .

Secondary aluminium production may especially be a large dioxin source. The European Dioxin Inventory gives an air emission factor of 22  $\mu\text{g I-TEQ/tonne}$  (range: 5-100 I-TEQ/tonne) of aluminium. The UNEP default emission factor for older plants is 150  $\mu\text{g TEQ/tonne of aluminium}$ .

Magnesium production has a large emission potential to both air and water, which had been first described in a Norwegian study. Modern plants have improved their performance though.

Shredders emit both PCBs and dioxins, but have only been scarcely examined yet. In Belgium (Flanders) large dioxin (and PCB) deposition campaigns were organised near many shredder plants. High depositions of dioxin and especially dioxin-like PCB's (DL-PCB's) were found. Emission measurements revealed that these pollutants were mainly dispersed by diffuse emissions. Dust control programs are initiated and the environmental impact is currently followed up by means of deposition measurements.

During the years, legal and illegal wire or cable reclamation have caused some dioxin pollution episodes (31,35-36,39). The default air emission factor for open cable burning is 5000  $\mu\text{g TEQ/tonne scrap}$  (50).



### 1.7.4 Power generation and heating

Power generation and heating cover important processes in society, with heating being more important in the northern countries with a colder climate. Fossil fuels are the most important fuels: coal, crude oil and natural gas. In some countries 'biomass' energy produced from straw or wood combustion is an important additional contribution. Biogas is only of minor importance. All these combustion processes may generate dioxin emission to the air and residues (ashes) as illustrated in Table 1.5.

**Table 1.5: UNEP Category 3: Power generation and heating, and UNEP emission factors ( $\mu\text{g TEQ/TJ}$ )<sup>5</sup>**

UNEP No.	SNAP Code	Subcategories	Air	Water	Land	Product	Residue
3a	10100	Fossil fuel power plants	0.5-35				14
3b	20300	Biomass power plants	50-500				15
3c	91006	Landfill, biogas combustion	8				X
3d	-	Household heating and cooking (biomass)	100-1500		(X)		10-1000/ tonne ash
3e	20200/20100	Domestic heating (fossil fuels)	1.5-12000		(X)		5000-30000 /tonne ash

"X" means not quantified

The use of fossil fuels such as natural gas and oil in modern large power stations for the generation of electricity is not a very significant source of dioxins. The European Dioxin Inventory gives air emission factors for natural gas of 0.02-0.03  $\mu\text{g I-TEQ/TJ}$ , corresponding to air emission concentrations of about 1  $\text{pg/Nm}^3$ . The UNEP emission factor is 1.5  $\mu\text{g I-TEQ/TJ}$ .

However, the use of coal as fuel may form more dioxins depending on coal quality and boiler function. UNEP gives a default air emission factor for coal of 10  $\mu\text{g TEQ/TJ}$ . The European Dioxin Inventory gives for coal air emission factors of 1-7  $\mu\text{g I-TEQ/TJ}$ , corresponding to 0.03-0.2  $\mu\text{g I-TEQ/tonnes coal}$ . A recent Danish investigation of a modern power plant reported an emission factor of about 0.03  $\mu\text{g I-TEQ/tonnes coal}$  and emission concentrations of less than 10  $\text{pg I-TEQ/Nm}^3$  (57).

In general, smaller industrial power plants, district heating plants and residential/domestic heating appliances using fossil fuels will not operate at complete combustion levels and will not have the same cleaning equipment as large power plants. The dioxin air emissions from these processes can, therefore, be ten to hundred times higher. Low-cost coal-fired stoves of Polish origin emitted 126  $\mu\text{g I-TEQ/tonne Polish hard coal}$  with a non-insulated chimney and ten times more with an insulated chimney indicating dioxin formation in the chimney. Concentrations of dioxin in flue gasses were between 6 and 115  $\text{ng/Nm}^3$  (11%  $\text{O}_2$ ) (58).

Based on German emission factors of 0.3-1.9  $\mu\text{g I-TEQ/tonne coal}$  the European Dioxin inventory estimates for residential heating an emission of 0.05-0.1  $\text{ng I-TEQ/m}^3$  natural gas and 0.02-0.09  $\text{ng I-TEQ/l gas oil}$ .

The situation can be even worse when using biomass fuels (wood and straw) in industry, district heating or in small boilers at farms and wood stoves. In small boilers and stoves a lower temperature and very little or no cleaning of flue gases are the usual operational conditions.

In the UK dioxin emission factors have recently been determined for domestic burning of coal and hard wood to be 3.0 and 0.21  $\text{ng TEQ/kg fuel}$ , respectively. It is relatively low levels (59).

Based on German data for industrial wood combustion, the European Dioxin Inventory estimates emission factors of 1-500  $\mu\text{g I-TEQ/TJ}$  or 0.02-10  $\mu\text{g I-TEQ/tonne wood}$ . A Danish study (57) of emissions from factories using wood chips reported results at the lower end of this range (0.02-0.3  $\mu\text{g I-TEQ/tonne wood}$ ). The chlorine content of untreated wood is usually between 0.001 and 0.01 wt%. The chlorine content in bark is 0.01 to 0.02%, and chipboard may contain about 0.2% chlorine if ammonium chloride is used as hardener (possible substitute: ammonium sulfate) (38). In the US, the emission factor for oak wood was 0.25  $\text{ng}$

<sup>5</sup> TJ: Terajoule ( $10^{12}$  Joule).

TEQ/kg used in wood stoves and 0.35 ng TEQ/kg used in fire places. In open fire places pine wood emitted 1.4 ng TEQ/kg natural and artificial logs emitted 2.4 ng TEQ/kg (60).

With respect to straw combustion the European Dioxin Inventory estimates dioxin emission factors of 17-50 µg I-TEQ/tonnes straw. Years ago a Danish study of farm boilers reported emission factors around 80 µg I-TEQ/tonnes straw but a newer study only measured 5-10 µg I-TEQ/tonne straw (57).

Modern district heating plants and combined heat and power plants using straw emit much less dioxins. A recent Danish study measured air concentrations less than 6 pg I-TEQ/Nm<sup>3</sup> and emission factors less than 0.05 µg I-TEQ/tonnes straw at such plants (57).

Dioxin content in residues is a particular and increasing problem in many instances, because the installation of filters decreases the air emissions but generates more contaminated filter dust. After combustion of straw in the UK, ashes contained 10-500 ng I-TEQ/kg ash. Burning of clean wood in Switzerland resulted in 0.6-8.5 ng I-TEQ/kg bottom ash and 720-7600 ng I-TEQ/kg filter ash. Fly ash from incineration of waste wood could contain up to 21 000 ng I-TEQ/kg ash.

Concerning wood stoves the European Inventory has estimated air emission factors of 1 µg I-TEQ/tonne for clean wood; 50 µg I-TEQ/tonne for contaminated wood and 500 µg I-TEQ/tonne for PCP contaminated wood. It may be rather difficult to estimate how much wood of the different types is actually burned, and if paper, carton, plastic etc. is added. Although the emissions from individual wood stoves are rather small, the total emissions from wood stoves will be significant. In a small country as Denmark it is estimated that up to 700 000 houses wood stoves are used and the current increase in oil prices and energy taxes might even lead to an increased use of wood stoves. Because the industrial and central amenities are more and more controlled, wood stoves may represent a relatively higher dioxin source in future.

The emissions of dioxins (and PAH and particles) from wood stoves have recently been studied in Denmark (61). In 2003, flue gas samples were collected direct from the chimney of twelve private wood stoves. There were great variations in emissions depending on type of stove and wood, and the way of operation. There was a tendency that newer stove models had lower dioxin emissions. The emission factors ranged between 0.3 and 17.7 ng I-TEQ/kg woods. By burning wastewood in stead of virgin wood in the same stove the dioxin emission became four times higher. The annual national emission based on burning virgin wood was estimated to 2-4 g I-TEQ.

Dioxin in chimney soot from wood stoves in Switzerland ranged from 500 to 9000 ng I-TEQ/kg soot. In a household heating system using a mixture of coal, wood and waste the dioxin levels could reach levels at 4-42 000 ng I-TEQ/kg soot.

### **1.7.5 Mineral products**

Due to the very high process temperatures during the production of cement, glass and bricks much of the eventual dioxin content of the raw materials is largely destroyed. Raw materials for production of mineral products, e.g. clay, may contain traces of dioxin. Samples of natural kaolin from Germany contained 3.9-1 132 ng I-TEQ/kg dry weight with a median of 154 ng I-TEQ/kg (62). Dibenzo-*p*-dioxins were the only congeners present, with OCDD being the main congener. No dibenzofurans have been determined. The distribution was:

2,3,7,8-TCDD	0.1-0.9 %
1,2,3,7,8-PeCDD	0.3-1.4 %
1,2,3,4,7,8-HxCDD	0.2-1.5 %
1,2,3,6,7,8-HxCDD	0.3-1.8 %
1,2,3,7,8,9-HxCDD	0.7-5 %
1,2,3,4,6,7,8-HpCDD	6.3-22.1 %
OCDD	67.6-92.4 %

In 1997 ball clay was the source of the dioxin contamination of chickens in the USA. The average dioxin contents in raw and processed clay samples were respectively 1513 and 966 ng I-TEQ/kg dry weight (63). Due to the very high process temperatures during the production of cement, glass and bricks much of the eventual dioxin content of the raw materials is largely destroyed. However, also in this process the formation of secondary dioxins has to be taken into account.

In Table 1.6 the default dioxin emissions factors from the production of mineral products are shown.

**Table 1.6: UNEP Category 4: Production of mineral products and ranges of emission factors ( $\mu\text{g TEQ/tonne product}$ ).**

UNEP No.	SNAP Code	Subcategories: Production of mineral products	Air	Water	Land	Product	Residue
4a	30311	Cement kilns	0.05-5				X
4b	30312	Lime	0.07-10				X
4c	30319	Brick	0.02-0.2				X
4d	30314/30315	Glass	0.015-0.2				X
4e	30320	Ceramics	X				X
4f	30313	Asphalt mixing	0.007-0.07			X	0.06
4g		Oil shale processing	0.003			0.07	2

"X" means not quantified

Cement kilns emit very low concentrations of dioxins to the atmosphere. However, the production flow is considerable; therefore it still may represent an important dioxin source. The emission of dioxins is somewhat higher, if waste oils, solid hazardous waste, fly ash etc. are added or used for co-incineration. The product may contain some residues.

Emission factors from cement kilns in the European Dioxin Inventory range from 0.05-5  $\mu\text{g I-TEQ/tonne}$  produced cement with 0.15  $\mu\text{g I-TEQ/tonne}$  as a default value. Older investigations reported concentrations of 0.02-1  $\text{ng/Nm}^3$  but recent Danish measurements from the only Danish plant resulted in <3  $\text{pg I-TEQ/Nm}^3$ . A new Spanish study reports that emission concentrations from cement kilns with additions of sewage sludge and waste tyres were 2-22  $\text{pg/Nm}^3$  or below the limit value of 100  $\text{pg/Nm}^3$  (64).

With respect to the production of bricks the European Dioxin Inventory estimates an emission factor of 18  $\text{ng I-TEQ/tonne product}$  (range: 1-230  $\text{ng I-TEQ/tonne}$ ).

With respect to the production of glass the European Dioxin Inventory estimates an emission factor in the range of 5-32  $\text{ng I-TEQ/tonne product}$ .

Burning of lime may emit dioxins. The European Dioxin Inventory gives emission factors ranging from 0.01-29  $\mu\text{g I-TEQ/tonne lime}$ .

In the Netherlands, asphalt-mixing processes especially with recycling of old asphalt were found to possibly emitting dioxins to the atmosphere. An emission factor of 47  $\text{ng I-TEQ/tonne asphalt}$  was estimated on the basis of a few measurements.

### **1.7.6 Transportation**

Transportation/traffic was one of the large dioxin sources when leaded petrol was used, because such fuels also contained 1,2-dichloroethane and 1,2-dibromoethane as scavengers. Therefore, halogens, organic matter and temperature determined the conditions for the formation of chlorinated dioxins, brominated dioxins and chlorobromodioxins. A typical emission factor was 70  $\text{pg I-TEQ per km driven}$ . The UNEP default factor is 2.2  $\mu\text{g TEQ/tonne fuel}$ .

Nowadays with non-leaded petrol and catalysts installed the dioxin contribution from cars is insignificant. Dioxin depositions measured in Belgium confirm that low dioxin levels are found at large traffic points. However, vehicles with 2-stroke engines or diesel fuel, and ships may still contribute dioxin emissions, because of the large numbers of vehicles and occurrence of chlorine in lubricating oils.

Recently, an average emission factor was developed for a diesel tractor: 29  $\text{pg I-TEQ/km}$  (65). Moreover, dioxin inventories have ignored that the use of leaded petrol in small airplanes is still allowed. As seen in Table 1.7, UNEP specifies in detail transport as an emission source, which has been neglected by most countries.

**Table 1.7: UNEP Category 5: Transport and ranges of UNEP emission factors ( $\mu\text{g TEQ/tonne}$ )**

UNEP No	SNAP Code	Subcategories for transport	Air	Water	Land	Product	Residue
5a	70100	4-Stroke engines	0-2.2				
5b	70500	2-Stroke engines	2.5-3.5				
5c	70200/70300	Diesel engines	0.1				(X)
5d	80300/80400	Heavy oil fired engines	4				(X)

"X" means not quantified

The importance of the chlorine content (additives) of lubricating oils for the dioxin emission from diesel vehicles has recently been studied. Typically, emission factors were 5-40 pg-I-TEQ/litre fuel and max. 160 pg I-TEQ/l. No connection with chlorine content in lubricating oils was found. When diesel oxidation catalyst was removed, the emissions were somewhat higher (66).

### 1.7.7 Uncontrolled combustion processes

Uncontrolled combustion processes will often involve high temperatures, organic matter and chlorine present as trace contaminant. Thus the potential conditions for dioxin formation are available. Dioxins are likely to spread with smoke and deposited far away from the source. It is also important to take into account that the type of water used to combat fire may contain increased levels of dioxins that may end up in soil, water, sewage plants or residues. Some UNEP emission factors are given in Table 1.8.

**Table 1.8: UNEP Category 6: Uncontrolled combustion processes and ranges default emission factors ( $\mu\text{g TEQ/tonne material}$ )**

UNEP No	SNAP Codes	Subcategories	Air	Water	Land	Product	Residue
6a	110300	Biomass burnings (forest, grassland, straw)	0.5-30	(X)	4-10		(X)
6b	90700	Landfill fires, accidental fires, open burning	60-1000	(X)	10-600		10-600

"X" means not quantified

Only a few countries take natural fires into account as a dioxin source; however, it is impossible to prevent dioxin emissions from natural fires. Air emission factors have been determined for forest fires to be between 15 and about 30 ng TEQ/kg material (67).

Dioxin emissions could be prevented with respect to accidental fires in factories, buildings, vehicles etc., where materials and equipment could be substituted with material not containing chlorine compounds. This has been partly achieved by banning PCB containing equipment and preservation of wood. With PCP, however, as long as halogenated polymers are being applied in building materials and consumer articles, and halogenated compounds are used as flame retardants, dioxin formation is likely to continue when accidental fires break out in dwellings where this material is present.

In the countryside it may be a common habit to burn household waste in a barrel in the garden. In the USA a recent investigation calculated air emission factors corresponding to 8-50  $\mu\text{g I-TEQ/tonne waste}$  (68). Another study of backyard burning gives a similar air emission factor range of 4-72 ng/kg, with a median of 20 ng WHO-TEQ/kg. PCB contributes to 5% of the TEQs, and PVC content in the waste increases the dioxin air emission tenfold (69). Belgium has performed a study to evaluate the impact of open burning of waste to the dioxin deposition levels. It appeared that the burning of waste can double the dioxin deposition value (161).

UNEP gives a much higher emission factor of 300  $\mu\text{g TEQ/tonne}$  for similar combustion; landfill fires having an estimated emission factor of 1000  $\mu\text{g TEQ/tonne}$  and accidental fires 400  $\mu\text{g TEQ/tonne}$ . Regards landfill fires the emission will depend on waste composition. In some countries land disposal of combustionable waste is not allowed. Japanese scientists have determined experimental emission factors for landfill fires to 23-46 ng/kg to air and 120-170 ng/kg to residue (70).

### 1.7.8 Chemicals and consumer goods

In Table 1.9 the UNEP subcategories concerning the production of chemicals and consumer goods are given. Neither of these subcategories are presently important sources but historically they are included in dioxin inventories.

**Table 1.9: UNEP Category 7: Production of chemicals and consumer goods and ranges of emission default factors (µg I-TEQ/tonne)**

UNEP No	SNAP Codes	UNEP Subcategories	Air	Water	Land	Product	Residue
7a	40602/3/4	Pulp and paper mills	0.07-0.2	0.06-4.5		0.1-30	0.2-50
7b	40400/40500	Chemical industry	0.0003-0.4	0.03-1	(X)	0.03-2000000	0.2-3000
7c	40100	Petroleum industry	8				X
7d	60312	Textile plants		X		0.1-100	
7e	60313	Leather plants		X		10-1000	

“X” means not quantified

Until a few years ago most paper and pulp industries used chlorine or hypochlorites as bleaching agents. Chlorine bleach paper mass can contain up to 40µg I-TEQ/tonne dry weight (recycled paper mass ten times less), and large amounts of dioxins were released especially to the aquatic environment. This was a major contribution to the dioxin inputs into the Baltic and to wildlife. Most industries have stopped using these bleaching agents and the present releases are negligible. Nevertheless, aquatic sediments influenced by such factories may still contain some dioxins.

The former use of bleaching agents containing chlorine has also been a problem in some textile and leather industries. Chemical industries producing pesticides, chlorine and organic halogenated chemicals, especially chlorophenols, are the classical dioxin pollution sources. Dioxin emissions from this kind of production plants still occur but have decreased substantially during the last years. A typical example of accidental pollution was the contamination in Seveso, Italy in 1976 caused by a dioxins cloud escaping from a plant producing trichlorophenol.

The vinyl chloride monomer (VCM) manufacturing industry has been discussed intensively as a dioxin source. OSPAR Decision 98/4 on “Emission and Discharge Limit Values for the Manufacture of Vinyl Chloride Monomer (VCM) including the Manufacture of 1,2-dichloroethane (EDC)” includes emission limit values of <0.1 ng I-TEQ/m<sup>3</sup> flue gas (<0.1 g I-TEQ per year) and <1 g I-TEQ/tonne of oxychlorination capacity. In comparison a modern chlorine plant and a VCM plant annually emits <0.05 g I-TEQ and <0.2 g I-TEQ respectively to the air.

The UNEP emission factors for old EDC/VCM processing plants are 1 µg TEQ/tonne to water. Modern EDC/VCM processing plants emit 0.4 µg TEQ/tonne to air, 0.5 µg TEQ/tonne into water, 0.03 µg TEQ/tonne into products and 10 µg TEQ/tonne into residues. A modern PVC plant emits 0.0003 µg TEQ/tonne into air, 0.03 µg TEQ/tonne into water, 0.1 µg TEQ/tonne into products and 0.2 µg TEQ/tonne into residues.

### 1.7.9 Miscellaneous

Some other possible dioxin sources are listed in Table 1.10.

**Table 1.10 UNEP Category 8: Miscellaneous sources and their emission factors ( $\mu\text{g TEQ/tonne}$  or as indicated)**

UNEP No	SNAP Codes	Subcategories	Air	Water	Land	Product	Residue
8a	-	Drying of biomass	0.007-10			0.1-0.5	
8b	90900	Crematoria (per cremation)	0.4-90				2.5
8c	-	Smoke houses	0.6-50			X	X
8d	60202	Dry cleaning		X		X	50-3000
8e	-	Tobacco smoking (per item)	0.1-0.3				

"X" means not quantified

For drying of green fodder (grass pills etc.) the European Dioxin Inventory gives an emission factor of  $0.1 \mu\text{g I-TEQ/tonne}$  material.

In the European Dioxin Inventory the emission factor for crematoria is reported as  $8 \mu\text{g I-TEQ/human remains}$  (range:  $3-40 \mu\text{g I-TEQ/human remains}$ ).

Use of candlelight is a recently discovered dioxin emission source indoors. Stearin or paraffin waxes may contain additives such as colour pigments with traces of dioxin or other substances promoting the dioxin formation. The emission factor is  $4-27 \text{ pg I-TEQ/kg wax}$  and the concentration in the emissions is up to  $0.04 \text{ pg I-TEQ/m}^3$  (41).

#### 1.7.10 Disposal/landfills

The disposal and land filling of waste as a dioxin source concerns mainly discharges to water and soil as shown in Table 1.11. The emission factors for sewage sludge and waste oil incineration are given in table 1.3 and discussed in section 1.5.1.

**Table 1.11: UNEP Category 9: Disposal/landfill and range of emission factors ( $\mu\text{g TEQ/m}^3$ )**

UNEP No	SNAP Code	Subcategories	Air	Water	Land	Product $\mu\text{g TEQ/t}$	Residue
9a	90400	Landfill and waste dumps		0.03-0.2	X		
9b	91001/91002	Sewage and sewage treatment	(X)	0.0001-0.002	X		10-1000
9c		Composting				5-100	
9d	-	Open water dumping		0.0001-0.005			
9e	-	Waste oil disposal (non thermal)	X	X	X	X	X

"X" means not quantified

A Japanese investigation has shown that dioxin may leach from landfills, especially if detergents are present as a carrier. Concentrations range from  $<0.001-50 \text{ pg I-TEQ/litre leachate}$  (71, 72).

Composting is a popular method of handling and using organic waste originating from households, gardening and agriculture and has been identified as a new UNEP subcategory. Compost made by green materials from non-polluted areas contains about  $5 \text{ ng I-TEQ/kg dry weight}$ . Typical kitchen and garden waste may be two to three times more contaminated, while other organic fraction may contribute twenty times more.

### 1.7.11 Hot spots

PCB containing transformers and other equipment should be phased out in all OSPAR countries (see also Polychlorinated Biphenyls (PCBs), OSPAR, 2001). Leakage from incorrectly labelled old equipment could give rise to serious accidental emissions. In Table 1.12 the emissions for hot spots are shown.

**Table 1.12: UNEP Category 10: Identification of Potential Hot Spots ( $\mu\text{g TEQ/tonne}$ )**

UNEP No	SNAP Code	Subcategories	Air	Water	Land	Product	Residue
10a	40524 a.o.	Production sites of chlorinated organics			X		
10b	40413	Production sites of chlorine			X		
10c	40525	Formulation sites of chlorinated phenols			X		
10d	60406 a.o	Application sites of chlorinated phenols	X	X	X	X	
10e	60406	Timber manufacture and treatment sites		X	X	X	X
10f	60507	PCB-filled transformers and capacitors				15000-15000000	X
10g	90400	Dumps of wastes/residues from categories 1-9	X	X	X		X
10h	-	Sites of relevant accidents		X	X		X
10i	-	Dredging of sediments					X
10j	-	Kaolinite and ball clay sites			X		

"X" means not quantified

### 1.7.12 Selection of most important sources

Based on the previous sections the main dioxin pollution sources are considered to be:

**To air:**

- Incineration of different kinds of waste and sludge;
- Heating of houses and farm with biomass (straw, wood) and coal, including wood stoves;
- Metal industry, especially sintering processes, reclamation of metallic waste and shredding;
- Accidental and natural fires;
- Engines of ships.

**To water:**

- Paper and pulp industries using chlorine;
- Waste water from chloroorganic industries;
- Textile washing and bleaching using chlorine;
- Landfill leakage;
- Atmospheric deposition.

**To soil:**

- Application of sewage sludge on agricultural land;
- Atmospheric deposition;
- Composting;
- Illegal cable burning;
- PCP treated timber.

**To residues:**

- PCB equipment and oils;
- Ashes from incineration and combustion processes.

For other compartments than air data is scarce and indicate a large uncertainty. Potential new sources of dioxins may still be discovered.

## 1.8 Pathways to the marine environment

The solubility in water of dioxins is extremely low, and in natural waters dioxins mostly occur associated with organic matter or films. There are only a few direct industrial point source discharges of dioxins to the aquatic environment. Waste water from households and smaller enterprises contain traces of dioxins, the major part of which ends up in sewage sludge produced by municipal sewage treatment works.

Besides some industrial point sources, such as older non-upgraded plants producing magnesium, PVC or paper and pulp, the most important direct source of dioxins to the aquatic and marine environment will probably be dry deposition of airborne particle-bound dioxins. The insignificant water solubility of dioxin means that coastal sediments are important sinks for dioxins in the aquatic environment.

## 2. Monitoring Data, Quantification of Sources and Assessment of the Extent of the Problem

### 2.1 Monitoring data

In comparison with many other environmental pollutants not many long-term monitoring exercises and investigations of dioxins exist. Thus good data are scarce and studies of trends are difficult to carry out. The explanation is of course that chemical analysis of dioxins is very time-consuming and costly. The rapid development of instrumental methods has increased the possibilities for congener-specific detection of ultra-trace levels in various new media but this made it difficult to compare with older results.

In Table 2.1.1 an overview of environmental matrices analysed in OSPAR States based on the 1999 study "Compilation of EU Dioxin Exposure and Health Data" (73) and other reports is shown. This information may not be complete.

**Table 2.1.1: Overview of environmental matrices analysed in OSPAR States**

	BE	CH	DE	DK	ES	FIN	FR	IRL	ISL	LUX	NL	NO	PT	SE	UK
Air	X	X	X	X	X					X	X	X		X	X
Soil	X	X	X	X	X	X		X		X	X	X		X	X
Vegetation		X	X			X	X				X				X
Water		X			X							X		X	
Sediment	X	X	X	X	X	X	X			X	X	X		X	X
Sewage		X	X	X	X										X
Wildlife			X			X								X	
Fish/shellfish			X	X	X	X	X	X			X	X		X	X
Cow milk	X	X	X		X		X	X			X				X
Breast milk			X	X	X	X	X				X	X		X	X
Human blood	X														
Deposition	X														

#### 2.1.1 Air

All PCDD/PCDF congeners have a very low volatility, thus in the atmosphere dioxins are mostly attached to fine or ultra-fine particles. The less chlorinated congeners are more abundant in the vapour phase than the highly chlorinated congeners.

Investigations from many European countries show that background levels in rural and unpolluted areas range from 0.01-0.05 pg TEQ/m<sup>3</sup> air. In larger cities levels may be ten times higher. Typical concentrations in Europe are 0.05-0.1 pg I-TEQ/m<sup>3</sup> (41). Atmospheric concentrations of 0.3 pg I-TEQ/m<sup>3</sup> or higher are indicative for local emission sources that need to be identified and controlled (74). One of the highest reported levels was about 15 pg I-TEQ/m<sup>3</sup> measured 150 m from a Welsh waste incinerator (73). In the Ruhr area in Germany air dioxin levels were reduced by 60% in the period 1987-1994 (75).

Since the fire in an office building in Binghampton, New York, 5 February 1981 it is well-known that dioxins may be formed during fire and be present in the soot covering the interior of the building. A famous European example is the fire at Düsseldorf Airport on 11 April 1996, where dioxin levels on surfaces were up to 334 ng I-TEQ/m<sup>2</sup>, and soot contained on average 43 µg I-TEQ/kg. The levels were much higher than the



German limit value for sanitation, which is 10 ng TEQ/m<sup>2</sup>. Some brominated dioxins were also identified. Those were formed when polystyrene foam insulation containing the flame retardant hexabromocyclododecane was burned (76).

Deposition of dioxins on surfaces outdoors after fires also occurs, and surface wipe samples are used as an emission indicator. A Danish guideline for sampling after fires exists (77).

The daily dioxin air depositions in rural, urban and industrial areas have been estimated to respectively 5-10, 30-40 and <1000 pg I-TEQ/m<sup>2</sup> (26). The annual atmospheric depositions of dioxins in Denmark (78), Germany (79, 80) and the Netherlands (81) have been estimated to 1-2, 3.8, 1-5 and 10 ng I-TEQ/m<sup>2</sup>, respectively.

The annual global deposition flux (82) has been estimated to range between 18 and 620 ng PCDD/F/m<sup>2</sup>. In more recent studies the annual atmospheric dry and wet deposition to the Atlantic Ocean were estimated to 9 and 45 ng PCDD/F/m<sup>2</sup>, respectively (83,84). It may be assumed that 1.5% of PCDD/F roughly corresponds to I-TEQ. Thus, an atmospheric deposition of 1 ng I-TEQ/m<sup>2</sup>/year is a reasonable estimate for the marine environment.

Belgium (Flanders) runs a large dioxin deposition network. The number of measurement stations increased from 10 in 1993 to 78 in 2000. (162) In 2006 samples are taken on 53 locations in different areas (rural, urban and industrial). Nowadays the highest dioxin depositions are measured near metal shredder plants (30-40 pg WHO-TEQ/m<sup>2</sup>.day). Peak values are also measured at other industrial locations (60-140 pg WHO-TEQ/m<sup>2</sup>.day). At rural and urban locations, the dioxin depositions are about 2 to 5 pg WHO-TEQ/m<sup>2</sup>.day. Dioxin deposition guide values were calculated. When the level of 26 pg WHO-TEQ/m<sup>2</sup>.day is exceeded, additional deposition samples are taken in order to get info about the temporal and spatial distribution of the dioxin pollution. The exceedance of the deposition value might lead to emission measurements performed by the Environmental Inspection and food analyses performed by the Flemish Agency of Food Survey (FAVV).

### **2.1.2 Soil**

The microbiological or chemical degradation of dioxins in soil is negligible. Studies have not detected any degradation during 10 years of dioxin presence (80). Because of the low solubility in water, dioxins are considered rather immobile in soil, and no measurable leaching will normally occur without adding detergents. Thus dioxin will concentrate in the topsoil layer (0-10 cm depth) but ploughing may mechanically disperse dioxin to other areas. The depth of sampling is therefore of great importance for the outcome of the studies.

The main sources of dioxins in soil are atmospheric deposition, waste disposal, application of sewage sludge and composting.

The dioxin levels in rural and agricultural surface soil are typically 0.1-5 ng I-TEQ/kg dry weight, and about ten times higher levels are found in urban soil. At polluted sites, e.g. near old incinerators, levels may be ten to hundred times higher than the background level. Even higher levels of 10 000-100 000 ng I-TEQ/kg soil (dry weight) have been determined in soil around a closed German metal reclamation plant and a Dutch cable burning site. The highest value is comparable with the levels found in polluted areas near the Seveso accident. For soils there will be no significant difference between I-TEQs and WHO-TEQs.

The mean dioxin levels in UK and Norwegian grass- and woodland soil (0-5 cm depth) were 4-30 ng I-TEQ/kg dry weight (85). Levels in soil in England have increased four times during the last 100 years (25). In Spanish soil (0-3 cm depth) dioxin mean levels were 0.16, 1.3, and 2.6 ng I-TEQ/kg dry weights in unpolluted, residential and industrial areas, respectively (86). In Danish topsoil (0-10 cm depth) the levels in rural areas were all <1 ng I-TEQ/kg dry weight. Soils from urban areas had higher contamination (87). The highest concentrations were found in soils from a park in Copenhagen (15 ng I-TEQ/kg) and a residential area downtown (20 ng I-TEQ/kg).

In 1992 German authorities set a preliminary reference (limit) value of 5 ng TEQ/kg dry weight for soil, where no sanitary measures need to be carried out. If levels are 5-40 ng TEQ/kg dry weight, monitoring should be carried out and soil with more than 40 ng TEQ/kg dry weight should not be used for agriculture. It was recommended that soil with ≥100 TEQ ng/kg dry weights should be removed from children playgrounds, soil with ≥1000 ng/kg dry weight should be removed from residential areas and soil with ≥10 000 ng TEQ/kg dry weight from all areas (80). Sampling depth is 30 cm for agricultural land, 10 cm for grassland and 2-10 cm for playgrounds.

In Switzerland the regulations are more stringent. At soil levels over 5 ng I-TEQ/kg dry weight pollution sources should be identified and emission controls implemented. At levels over 20 ng I-TEQ/kg dry weight

cow milk should be investigated to identify if the normal background load (>5 ng I-TEQ/kg butterfat) is increased significantly. At 100 ng I-TEQ/kg dry weight children playground should be sanitised, and at 1000 ng I-TEQ/kg dry weight soil sanitation should be carried out for gardens and agricultural fields (88). The oral bioavailability of dioxin in soils has been estimated to about 25% (89).

In Belgium a study was performed to calculate guide values for dioxins and DL-PCB's in soil (163). The preliminary values for the total of dioxins and DL-PCB's are 3 ng WHO-TEQ/kg dw on background locations, 9 ng WHO-TEQ/kg dw on agricultural land, 65 ng WHO-TEQ/kg dw in residential areas, 260 ng WHO-TEQ/kg dw in recreation areas and 1600 ng WHO-TEQ/kg dw in industrial areas. Soil samples were taken in areas where high dioxin depositions were measured. The values of the total of dioxins and DL-PCB's ranged between 1 and 26 ng WHO-TEQ/kg dw. The samples with low TEQ-values were probably taken on tilled soil (164).

### **2.1.3 Vegetation**

The main dioxin contamination of the natural vegetation is atmospheric deposition on plant leaves.

The background concentration of dioxin in vegetation from non-polluted areas is <1 ng/kg dry weight. Typical concentrations in grass in northern Switzerland were 0.2-4 ng I-TEQ/kg dry weight (41). An older British study of hay samples showed a time trend over 100 years. The level in the 1890s was 12 ng PCDD/F per kg dry weight (corresponding to 0.2 ng I-TEQ/kg dry weight) with 40 ng PCDD/F per kg dry weight in the 1950s, a maximum of 97 ng PCDD/F per kg dry weight (corresponding to 1.5 ng I-TEQ/kg dry weight) in the 1960s and a decline to 85 ng PCDD/F per kg dry weight in 1980 and 38 ng PCDD/F per kg dry weight (corresponding to 0.5 ng I-TEQ/kg dry weight) in 1990 (25).

In polluted areas the surface of plants and fruits may contain much more dioxin. Around an Austrian copper smelter dioxin levels in pine needles and grass were respectively 85 and 20 ng I-TEQ/kg dry weight (56). The accumulation of dioxins depends on vegetation type. Green cabbage, which has a large enclosed surface, accumulates for instance 30 times more dioxin than lettuce. Deposition of 56 pg TEQ/m<sup>2</sup> from the air (polluted area) resulted in a soil content of 75 ng TEQ/kg dry weight, a lettuce content of 2.4 ng TEQ/kg dry weight, a grass content of 28 ng TEQ/kg dw and a green garbage content of 65 ng TEQ/kg dry weight (80). In the neighbourhood of an incinerator in Switzerland the transfer factors from deposition to grass and to cow milk were respectively 0.4 and 0.02 ng TEQ/kg dry weight (41).

The direct uptake of dioxin from soil by plant roots depends on the water solubility of the congener and is normally very low or negligible, and the dioxin will accumulate near the inner surface, for instance in the peel of potatoes. However, some species such as cucumber, zucchini and pumpkins have a rather high uptake and wider transfer in the plant (90). The upper bound levels of dioxin in Dutch summer vegetables were <10 pg TEQ/kg fresh weight, and the levels were ten times higher in winter vegetables, highest with 122 pg TEQ/kg fresh curly kale (91).

Even when the soil is much polluted the dioxin levels in vegetation are rather low. For instance, lettuce grown on soil containing 13 000 ng I-TEQ/kg dry weight had only leaf concentrations of 4 ng I-TEQ/kg dry weight, corresponding to a transfer factor of 0.03% (80).

### **2.1.4 Water and sediment**

Trace levels of dioxins occur widespread in the aquatic environment. The extremely low water solubility of dioxins, which decreases with the degree of chlorination, results in extremely low background concentrations of dioxins in natural waters. In water samples from the Baltic the dioxin concentration were 1.8 fg N-TEQ/L in the particle fraction and 1 fg N-TEQ/L in the dissolved fraction (92). In the River Elbe the concentration upstream of Hamburg was 4 fg I-TEQ/L and downstream of Hamburg 17 fg N-TEQ/L. In the particulate water fraction the levels were 70-700 times higher and highest upstream (3.1 pg I-TEQ/L) than downstream (1.2 pg I-TEQ/L) (93).

In Switzerland typical dioxin concentrations were estimated at 1-2 pg I-TEQ/L in collected rain water from roofs and 3-7 pg I-TEQ/L in street run-off water (4126). Levels in street run-off water and storm water have also been measured at 3-20 pg I-TEQ/L, the higher concentration of which occurred in a large city (9457). Waste water from households contained about 30 pg I-TEQ/L. The levels in waste water from washing machines were a little lower (15-25 pg I-TEQ/L) (41).

There should be no risk of contamination of groundwater reservoirs from soil pollution, if dioxin is only present. However, in practice dioxin may leach from landfills. In Spain, leachate from eight different landfills contained 1.6-1520 pg I-TEQ/L (95).

The low water solubility means that only a slow spreading of dioxins in the aquatic environment occurs. Thus, the main parts of the anthropogenic dioxins released to marine waters will be detained in coastal zones concentrated in sediments. The background level in marine sediments is around 1 ng I-TEQ/kg dry weight but 10-100 times higher levels have been determined close to industrial pollution sources. Almost no degradation of accumulated dioxins occurs in such sediments, and the half-lives of dioxin congeners may be hundreds of years (96). The bioavailability of sediment-associated dioxins depends of various factors such as lipophilicity, molecular size and steric factors of the chemical and sediment characteristics such as organic carbon content, particle size and polarity of organic carbon (97).

In an older Norwegian investigation, dioxin in marine sediment samples from Svalbard and Barent Sea were  $\leq 1$  ng N-TEQ/kg dry weight (98). In Skaggerak, the North Sea and non-polluted fjords levels were up to 12 ng N-TEQ/kg dry weight, in harbour sediments 20-40 ng N-TEQ/kg dry weight and up to 60 000 ng N-TEQ/kg dry weight in heavily polluted fjords.

In three areas of Spain (Almeria, Barcelona and Tarragona), dioxin in coastal sediment ranged from 0.3 to 75 ng WHO-TEQ/kg dry weight. Coplanar PCBs were included and contributed to 1 to 84% of the TEQs, highest in Tarragona (99).

At the Belgian coast of the North Sea/English Channel sediment samples from five places were investigated. The dioxin concentrations ranged from 0.12 to 3.2 ng WHO-TEQ/kg dry weight without PCBs and 0.22-3.3-ng WHO-TEQ/kg dry weight included PCBs (100). In another study of sediments at the Belgian Coast using the CALUX-assay the highest concentrations were from the Schelde mouth: 2800-7200 ng Calux-TEQ/kg sediment (101). High levels were also found in the harbours of Zeebrugge (1600-4200 ng/kg) and Nieuwpoort (600-2200 ng/kg). These concentrations are much higher than coastal stations (250-710 ng/g).

In sediment from the river Elbe near Hamburg the dioxin levels were 41-73 ng I-TEQ/kg dry weight. In harbour sediment from Hamburg levels were up to 1500 ng I-TEQ/kg dry weight (80). Sediment from the river Rhine in the Netherlands close to PVC plants contained 433-922 ng I-TEQ/kg dry weight (102). Storm water sediment from Germany contained 10-29 ng I-TEQ/kg dry weight (103). Heavily polluted aquatic sediments may contain up to 80 000 ng I-TEQ/kg dry weight (73).

Analysis of dioxins and dioxin-like chemicals in sediments by the CALUX<sup>®</sup> bioassay (see Section 1.3) has been undertaken. In sediment samples (0-10 cm depth) from various U.K. estuaries the concentrations ranged 1.0-106 ng CALUX-TEQ/kg dry weight. In 24 out of the 35 sites/samples the levels were above a national Dutch guideline value from 1996 of 13 ng TEQ/kg (104). In the Netherlands 257 marine harbour sediment samples levels ranged 0.2-136 ng CALUX-TEQ/kg dry weight. PCDD/Fs explained 50% of the Calus activity. Management decisions in the Netherlands on the clean-up of hot spots are based on chemical analysis. If sediment is found to contain more than 1000 ng TEQ/kg dry weight, a statutory obligation exists to take remedial action. Quality guidelines for DR-CALUX activity in marine harbour sediments have been proposed (105):

<b>Guideline</b>	<b>ng TEQ/kg dry weight</b>
Target value	2
Screening value	15
Threshold value	25-50
Maximum value	1000

### 2.1.5 Fish and other aquatic organisms

Dioxins are highly liable to bioaccumulate in various aquatic organisms with bioconcentration factors of 2000-9000. Therefore, fish and shellfish are frequently used as biomonitors for the aquatic environment.

Dioxin levels in fish depend on the species, age/size and area. The highest levels of dioxin in fish muscle are found in fatty fish such as herring and salmon. Levels in cod, a less fatty fish, are typically ten times lower than in herring on a fresh weight basis but on fat basis the dioxin concentrations will often be very similar between various fish species. Skinned fillet accumulates approximately 30% of the total dioxin content of a salmon fish (106). There is a clear association between the age/size of a fish and the dioxin content (107).

Dioxin levels in herrings from the North Sea are typically 1-2 ng WHO-TEQ/kg fresh weight, which is a little less than levels in herrings from unpolluted Norwegian fjords and the western part of the Baltic Sea but 5 times less than in the northern and central Baltic Sea (108).

Some years ago the dioxin levels in perch from the Gulf of Botnia were around 20 ng I-TEQ/kg fresh muscle tissue within a 5 km distance from a Swedish pulp and paper factory using chlorine (109). Another study showed higher dioxin levels (6.7-9.0 ng TEQ/kg fresh weight) in herrings caught east of the Danish island Bornholm than west of this island (1.8-3.4 ng TEQ/kg fresh weight). Levels in the less fatty fish cod were much lower (<0.2 ng TEQ/kg fresh weight) (110). In a newly Finnish study of 111 pooled fish samples from the Baltic Sea, the EU limit value of 4 ng WHO-PCDD/F-TEQ/kg fresh weight was exceeded in 21 herring-, 8 salmon-, 3 river lamprey-, 2 perch- and one white-fish sample. Skinned samples had 12% lower levels than unskinned (111).

Dioxin levels in Norwegian marine fish and shellfish from polluted and unpolluted fjords and the North Sea are shown in table 2.1.2.

**Table 2.1.2: Dioxin levels (ng N-TEQ/kg fresh weight) in Norwegian marine fish and shellfish from polluted and unpolluted fjords and the North Sea (98)**

	Cod liver	Cod fillet	Flounder fillet	Eel fillet	Herring fillet	Mackerel	Edible Crab, claw meat	Shrimps	Common mussel
Polluted fjord	506	1.91	9.91	41.07	-	-	44	20	5.45
Unpolluted fjord	5.6	0.07	0.40	1.39	2.66	2.6	5.5	0.35	0.20
North Sea	-	-	-	-	1.5-2.0	0.8	-	-	-

A new investigation of dioxin in cod liver from the much polluted Frierfjord shows a downward trend in levels from about 10 000 ng TEQ/kg fresh weight in 1990 to about 500 ng TEQ/kg fresh weights in 2001 (112).

In eels from the Netherlands, levels of 1.2-9 ng TEQ/kg fresh weight were once found (113). A newer study reports 0.3-7.9 ng PCDD/F-TEQ/kg wet weight in wild freshwater eels, 0.9-3.1 ng PCDD/F-TEQ/kg wet weight in farmed eels and 0.2-3.0 ng PCDD/F-TEQ/kg wet weight in imported eels (114). If dioxin-like PCBs are included levels were 3-7 times higher. The CALUX bioassays gave results comparable with the chemical method for the total TEQ levels.

In the marine flatfish dab (*Limanda limanda*) from the French part of the English Channel, dioxin levels in muscle ranged from 7.3 to 14.2 ng/kg dry weight in March and from 2.7 to 6.0 ng/kg dry weight in September (115). Levels in livers were between 11 and 40 times higher. Highest levels were found at Seine Bay. Including PCBs, the levels in fish muscle were 0.655 ng fish-TEQ/kg wet weights at Seine Bay and 0.473 ng fish-TEQ/kg wet weights for Somme Bay. The levels expressed in WHO-TEQ were about 3 times higher.

Dioxin in marine mussels was monitored at the French coast in 1981-2004 (116). Levels of PCDD/Fs ranged 3.3-6.0 ng WHO-TEQ/kg wet weight at the English Channel, 0.7-2.0 ng WHO-TEQ/kg wet weight at the Atlantic coast and 0.4-1.9 ng WHO-TEQ/kg wet weight at the Mediterranean Sea. During the years there was a downward trend in levels. Dioxin in marine mussels was monitored at the French coast in 1981-2004 (116). Levels of PCDD/Fs ranged 3.3 – 6.0 ng WHO-TEQ/kg wet weight at the English Channel, 0.7-2.0 ng WHO-TEQ/kg wet weight at the antic coast and 0.4-1.9 ng WHO-TEQ/kg wet weight at the Mediterranean Sea. During the studied period, there was a downward trend in levels, with a time required to decrease by a factor of 2 being between 10 and 14 years.

A recent paper surveying organic contaminants in farmed and wild salmon started a debate about the safety of farmed fish (117). The dioxin levels in wild salmon from around the World were less than 0.5 ng WHO-TEQ/kg, while the farmed contained 1-3 ng WHO-TEQ/kg. About 75% of the WHO-TEQs were due to the dioxin-like PCBs included. In the Baltic Sea area with much higher pollution level farmed salmon have 10 times lower contamination of dioxin than wild salmon (110).

Dutch fishery products from the Atlantic Ocean, the Celtic Sea, the English Channel and the North Sea had an average of dioxin content of 1, 2, 5 and 2 ng WHO-TEQ/kg fresh weights, respectively (118). Dioxin-like PCBs contributed on an average 69% to these TEQ levels.

The Greenland shark (*Somniosus microcephalus*) is with a length of 7 metre the largest fish in arctic waters. Dioxin levels in the liver (range: 12-330 ng WHO-TEQ/kg fat; median: 82 ng WHO-TEQ/kg fat) are thirty times higher than the muscle (range: 0.44-7.5 ng WHO-TEQ/kg fat; median: 2.5 ng WHO-TEQ/kg fat) (120). Including PCBs, the medians were 87 ng WHO-TEQ/kg fat and 490 ng WHO-TEQ/kg fats, respectively. In muscle tissues PCBs contribute 30 times more than dioxin but in liver tissue only 5 times (119).

Marine mammals high in the food chain contain much dioxin. Dioxin concentrations in blubber of ringed seals from the Baltic Sea were about 170 ng WHO-PCDD/F-TEQ/kg lipid weights (120). In similar species caught near Svalbard, levels were about 5 ng WHO-PCDD/F-TEQ/kg lipid weights.

### 2.1.6 Terrestrial wildlife and birds

Only a few investigations of dioxin in terrestrial wildlife and birds exist. The levels are generally low, because these animals are foraging in rural areas. In Finland, however, levels of 830-66 000 ng I-TEQ/kg fat were determined in fish-eating white-tailed sea eagles (73). In pooled liver samples from Canadian Arctic seabird in 1993 the dioxin levels were 382, 615, and 6837 ng WHO-PCDD/F-TEQ/kg lipid weight in thick-billed murre (*Uria lomvia*), black-legged kittiwake (*Rissa tridactyla*) and norther fulmar (*Fulmaris glacialis*) (121). More recently dioxin in livers sampled from 16 fulmars in 2003 at Faroe Islands showed mean levels of 2210 ng WHO-PCDD/F-TEQ/kg fat and a range from 672-4900 ng WHO-PCDD/F-TEQ/kg fat (122).

Archived eggs of herring gulls collected from 1988-2003 from two North Sea islands and on Baltic Sea island were surveyed in Germany (123). There was a downward trend with somewhat lower levels in recent years. Levels were highest in the North Sea eggs with up to 366 ng TEQ/kg fat in 1988. Recent levels were >200 ng TEQ/kg fat in eggs from one of the North Sea islands but only the halv in the two other islands.

After the Seveso accident high levels were found in mice (4500 ng I-TEQ/kg bw) and in earthworms (12 000 ng I-TEQ/kg bw) (41).

### 2.1.7 Domestic animals

Cows and other domestic animals grazing close to sources of significant pollution may have increased dioxin levels in their body and milk (124). This is primarily due to increased levels of dioxin in the vegetation, and not by increased levels in the soil, especially with respect to cows, which have a low soil intake.

The background levels in cow milk in Ireland were 0.13-1.5 ng I-TEQ/kg fat. In France levels ranged from 0.32-8.37 ng I-TEQ/kg fat, including samples taken in the vicinity of municipal solid waste incinerators (73). Some years ago in the neighbourhood of a municipal solid waste incinerator in the Netherlands, cow milk contained up to 13 ng I-TEQ/kg fat, whereas background levels were below 2.5 ng I-TEQ/kg fat (81). In Austria, cows grazing close to a metal shredder had milk fat levels of up to 69 ng I-TEQ/kg which represents fourteen times the background level (56).

In Switzerland the dioxin content of cow milk from industrial dairies analysed in 1990/91 were between 1 and 1.8 ng I-TEQ/kg lipids and in 2001 between 0.32 and 0.85 ng I-TEQ/kg lipids (information submitted by the Swiss OSPAR delegation).

Concerning free range poultry, dioxin levels in soil have a big impact. At levels of 1-2 ng I-TEQ/kg dw eggs from free range hens may contain 2-6 ng I-TEQ/kg fat or up to four times more than in hens kept in stables/cages which are only exposed to non-polluted food (1.3-1.5 ng I-TEQ/kg fat) (41). A recent publication shows that the current soil levels of dioxins and DL-PCB's in residential an agricultural areas in Europe appear to be often too high to produce free-range eggs with dioxin levels below the current limit values in the EU. (165).

Some incidents of dioxin contamination in food have occurred. In late 1997 it was discovered that milk and butter in Germany had elevated levels of dioxin (average value in milk: 4 ng/kg fat) (125). This was caused by food containing citrus pulp pellets originating from Brazil. These pellets contained an average dioxin level of 6.5 ng I-TEQ/kg dry weight. In 1998 the European Commission set a maximum residue level of 0.500 ng/kg for such material (126; see also section 4.2.8).

In spring 1999, during the PCB and dioxin contamination of food in Belgium, the maximal dioxin level was above 1000 ng/kg fat. Poultry was most affected with levels up to 2600 ng I-TEQ/kg fat (127).

A review of the pathways of dioxins in the food chain from food has been published on the EU website (128).

Farm manure contains 1-4 ng I-TEQ/kg dry weight (41).

### **2.1.8 Food**

The most important dioxin exposure of the general public is through food. Fish, meat and dairy products contain considerable dioxin levels and contribute mostly to human exposure.

Fish on the European consumer market may contain up to 700 ng I-TEQ/kg fat but the typical range is 3-20 ng I-TEQ/kg fat (73,80). These levels are much higher than those found in terrestrial animals such as cattle, pigs and poultry. For instance, meat on the German market contains 0.5-3 ng I-TEQ/kg fat (80). For fish, the PCB contribution to the total-TEQ is, in general, higher than the contribution of PCDDs and PCDFs together, as was shown in section 2.1.5.

In Italy food of animal origin the dioxin content ranged 0.003-1.66 ng TEQ/kg fresh weight with a mean value of 0.14 ng TEQ/kg fresh weight (129). The main sources of human intake of dioxin were fish and cows milk.

In Finland dioxin in commercial milk in glass bottles was on average 0.83 ng TEQ/kg fat (130). In Germany commercial milk in 1992 contained 1.8 ng I-TEQ/kg fat but it has decreased to below 1 ng/kg in the following years (131).

Studies during the years have shown that commercial milk stored in cardboard may contain up to 20 times more dioxin than milk stored in glass bottles. Use of chlorine bleached coffee filter may also increase the dioxin intake.

In a recent survey of dioxins in milk, milk products and eggs from west European countries the dioxin content of the 138 milk and milk products were between 0.11 and 1.33 ng WHO-TEQ/kg fat with a mean of 0.35 ng WHO-TEQ/kg fat; including PCBs the mean raised to 0.98 ng WHO-TEQ/kg fat (132). In the 45 eggs the dioxin content ranged 0.14-1.2 ng WHO-TEQ/kg fat with a mean of 0.37 ng WHO-TEQ/kg fat; including PCBs the mean was 0.69 ng WHO-TEQ/kg fat, thus PCBs are relatively more important in milk than in eggs.

Average daily intakes of dioxins in EU countries range between 0.4 and 2.4 pg WHO-PCDD/F-TEQ/kg bw. In Finland, Sweden, France, Austria and Spain (Catalonia) the daily intakes were 0.8, 0.7, 0.5, 2.4 and 0.8 pg WHO-PCDD/F-TEQ/kg bw, respectively (133-137). The intake may double, if dioxin-like PCBs are included.

### **2.1.9 Indoor air**

Dioxin levels in indoor air are usually a little higher than in outdoor air. During several years concentrations of 1-3 pg TEQ/m<sup>3</sup> have been determined in houses and kindergartens containing wood treated with pentachlorophenol (PCP) (138).

In Germany, an average concentration of 101 ng I-TEQ/kg and range of 8-332 ng I-TEQ/kg was found in dust in residential dwellings. In dwellings contaminated with PCP, the average concentration was 1390 ng I-TEQ/kg (139).

After fire outbreaks in buildings, indoor surfaces will contain <200 ng I-TEQ/m<sup>2</sup>, and not more than 10 000 ng I-TEQ/m<sup>2</sup>. During fire outbreaks in industrial production or storage facilities more dioxin may be formed and released. Surface concentrations are about >100 000 ng I-TEQ/m<sup>2</sup> (80).

With respect to sanitation projects, Germany recommends that for surface concentrations of 10-150 ng TEQ/m<sup>2</sup> cleaning should be carried out and the submission of further information is required. During cleaning, skin contact should be avoided. Concentrations of 150-1000 ng TEQ/m<sup>2</sup> require cleaning by specialists and controlled disposal of cleaning liquids. Afterwards, control measurements and eventually more cleaning have to be performed. If concentrations are above 1000 ng TEQ/m<sup>2</sup>, the area has to be evacuated and isolated until cleaning is finished (139).

### **2.1.10 Workplace air**

In some industries workers are exposed to high dioxin concentrations. In steel works, metal recycling industries and waste incinerators air concentrations may range from 1 pg I-TEQ/m<sup>3</sup> to >50 pg I-TEQ/m<sup>3</sup> (the common occupational limit value) during a short period of time.

### 2.1.11 Humans

Dioxin accumulates in humans and concentrates mainly in adipose tissues. The residence time is decades, because the metabolism is negligible and the excretion is extremely low (with the exception for women with breast milk during a nursing period). Therefore, the normal daily intake of dioxin is larger than the daily elimination, and dioxin concentrations in the body will magnify over the years. On a lipid basis, individual levels of dioxins in blood, adipose tissue and breast milk are about the same. Typical levels of dioxins in adipose tissue are 10-50 ng I-TEQ/kg fat. In 1996, the average blood level in EU was 16.5 ng I-TEQ/kg fat (73).

The WHO has coordinated three rounds of international exposure studies of dioxins (and PCB) in human breast milk. The first round in 1987-88 covering Europe only showed dioxin levels of 8-40 ng I-TEQ/kg fat with an average of 22 ng I-TEQ/kg fat, or, ten to twenty times more than cow milk (140). Results from the 1992-93 study were about 35% lower (141). Special high levels was related to well-known dioxin sources and, the breast milk of a woman living in Germany close to a cable burning facility, contained levels of 125 ng I-TEQ/kg fat. In the third round from 2001-2003 more countries outside Europe were involved (142). In total 26 countries participated. The median levels in human breast milk ranged from 3.3 ng WHO-PCDD/F-TEQ/kg fat in Fiji Island to 22 ng WHO-PCDD/F-TEQ/kg fat in Egypt. Highest median levels in Europe were in Belgium and the Netherlands with 17 and 18 ng WHO-PCDD/F-TEQ/kg fat, respectively. Among the 16 European Countries participating in the study the average median was 11 ng WHO-PCDD/F-TEQ/kg fat. Some countries investigated the trend of dioxin levels in human breast milk. Sweden has carried out the longest monitoring programme and the most comparable (same laboratory) human breast milk investigations. A small downward trend has been detected but that trend is very small compared to the much larger decrease of levels of chlorinated pesticides. Germany detected a higher decline in levels (>10% per annum) but the levels were also higher at the beginning than in Sweden. Data collected more recently are given according to the WHO-TEQs, which results to some extent in higher levels. If the contribution from coplanar PCBs is also included, breast milk levels expressed in WHO-TEQs will be about two fold higher than in I-TEQs. Belgium has recently set up a monitoring program for human blood for different groups in the population.

## 2.2 Quantification of sources

Information on emissions of dioxins has been compiled based through information submitted by Contracting Parties. As techniques and effort to assess emissions have varied over time and were developed independently, this has resulted in various degree of consistency and comparability. Nevertheless, the data presented in the Background Document allow the formulation of reduction and monitoring strategies in the OSPAR regime.

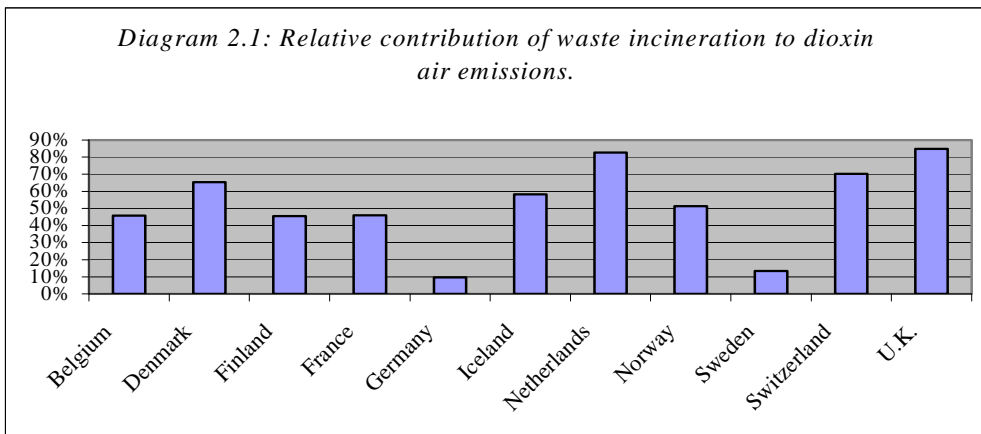
Emission data for OSPAR Contracting Parties have been compiled and made available through the [Convention on Long Range Transboundary Air Pollution](#) as part of its [EMEP programme](#). Under the Stockholm Convention new reporting has also started.

### 2.2.1 Waste incineration

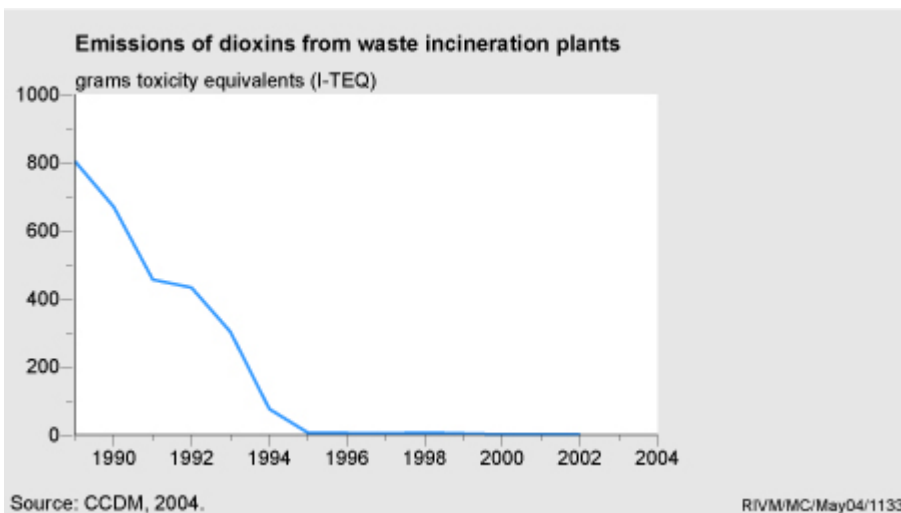
During the last decades waste incineration and filter technology have improved considerably. Ten years ago, air emission factors of 25 µg I-TEQ/tonne waste, average air emission concentrations of 5 ng I-TEQ/Nm<sup>3</sup>, and emission fluxes of 0.5 mg I-TEQ/hr were common with respect to municipal waste incineration, whereas concentrations ten times higher were found from municipal waste incinerators 30 years ago and small hospital incinerators ten years ago. Dioxin levels in the residues have also decreased with the new technology. In Germany, the average level in fly ash decreased from 13 000 to <1000 ng I-TEQ/kg, and in bottom ash from 50 to 5-20 ng I-TEQ/kg.

Countries such as Germany and Austria were implementing an emission standard of 0.1 ng I-TEQ/Nm<sup>3</sup> (at 11% O<sub>2</sub>) ahead of time, which was recently also established in all 15 EU Member States under EU Directive 2000/76/EC. With the application of the newest available technology for such plants it has been possible to obtain emission concentrations ten times below this standard. This implies that waste incineration processes are currently changing from being a very significant dioxin air pollution source to an insignificant one.

Diagram 2.1 illustrates the differences in contributions from waste incineration between OSPAR States based on a UNEP report of 1999 summarising the available information on releases of dioxins and furans to the environment (30). Data from Iceland were initially collected for the LRTAP Convention. Since the UNEP report much new technology have been introduced to better control emissions and an EU emission limit value enforced.



It should be noted that extent and practice of waste incineration varies between countries, e.g. in Finland this disposal method is rarely used. The dioxin emissions to air due to waste incineration are rather low in Germany as explained above. The low contribution in Sweden is due to a lesser use of waste incineration. The data is to some extent outdated because several countries, including Denmark, have introduced new technology since then. It is a matter of time before the contributions from most countries are similar to that in Germany. In the UK the estimated emission of dioxins from municipal waste incineration has for instance declined from 602 g in 1993 to 11 g (or 3% of the total emissions) in 1997 (43) and 2 g (or <1%) in 1999 (Information submitted to OSPAR for the purpose of this report.). In Belgium, the relative contribution of waste incineration was reported to be 5.4% in 2004. In the Netherlands the emission came down to zero in 2002 (see Figure) (143).



From 2003 to 2005 the emissions in Denmark decreased from 11 to 0.5 g TEQ, respectively (144).

In Table 2.2.1 the most recent estimated annual air emissions for the UNEP Category 1 sources from different OSPAR States are presented.

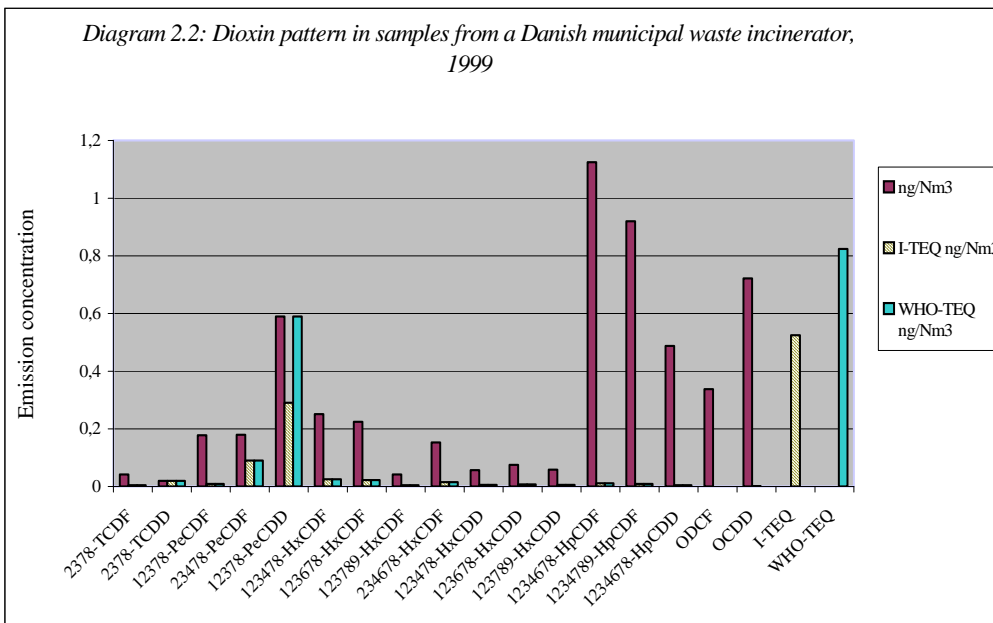


**Table 2.2.1: Estimated annual air emissions (g TEQ) from waste incineration in OSPAR countries.**<sup>6</sup>

UNEP Category 1: Waste incineration	BE 2004	DK 2005 (144)	FIN 2003 (49)	FR 1995	DE 1995	NL 2002 (143)	NO 2004 (145)	SE 2004 (45)	CH 2002 (49)	UK 2003 (47)
Municipal solid waste	0.040	0.5	2.4	227	30	0	0.6	1.1	5	
Hazardous waste	0.094	<0.03		2	2			0.025	2.5	0.07
Medical waste					0.1					1
Light-fraction shredder waste										
Sewage sludge	0.070					<0.1				0.07
Waste wood and waste biomass									0.7	
Destruction of animal carcasses										0.25
Industrial waste	3									

In addition, a Spanish study of 8 municipal waste incineration facilities operating during 1997-1999 showed a total annual emission of 1.1 g I-TEQ (146).

Diagram 2.2 shows an average dioxin pattern of emission samples from a smaller Danish municipal waste incineration plant (147).



In this example the sum of WHO-TEQs is 36% higher than the sum of I-TEQs. Co-incineration of clinical waste with municipal waste, which is quite common in Denmark, did not change anything with regard to air emissions of dioxin from this plant.

### 2.2.2 Ferrous and non-ferrous metal production

In Table 2.2.2 the annual emissions (g I-TEQ) from metal production in OSPAR countries are shown.

<sup>6</sup> Some data from the UK and Finland in this and/or following tables have been submitted by Contracting Parties to OSPAR in January 2002 for the purpose of this report.

**Table 2.2.2: Annual dioxin emission estimates (g I-TEQ) from UNEP Category 2: Ferrous and non-ferrous metal production in OSPAR Countries**

UNEP Category 2: Subcategories	BE 2004	DK 2002 (46)	FIN 2003 (49)	FR 1995	DE 1995	NL 1991	NO 2000	SE 2004 (45)	CH 2002 (49)	UK 2003 (47)		
Iron ore sintering	18.05		4.6	93	168	26	5.2	5.9- 8.6	0.34	26		
Coke production						0.3					0.3	
Iron and steel production and foundries		0.1-2.4			39.4	3.1				0.14	8	
Copper production					10						1	
Aluminium production		0.3			11.5			0.3			8.3	
Lead production											4.7	
Zinc production					7							
Brass and bronze production							91.6	4		5.6- 10.3	0.3	
Magnesium production									1.3			0.14
Other non-ferrous metal production						200			3.1			0.36
Shredders				0.007							0.2	
Thermal wire reclamation				0.005-5				1.5				
Others				<0.5								

Due to the fact that every country uses its own way to identify and specify the sources, it is very difficult to compare the figures. In principle though, countries with a large metal industry (ferrous and non ferrous metal production) have a very significant dioxin source, which has a high potential for reduction improvements. In Belgium, a clear decreasing trend is noted. Aluminium production, especially secondary aluminium production, is a possible important dioxin source. At a Danish plant high emission concentrations of 180 ng I-TEQ/Nm<sup>3</sup> were measured in year 2000 (148). When this plant was improved, emission concentrations were reduced to levels much less than 0.1 ng I-TEQ/Nm<sup>3</sup>.

In a Norwegian plant emissions of 0.1 and 9 mg TEQ/tonne magnesium produced have been measured to air and water, respectively. A French factory of the same company emits 1000 times less (149). In the period 1998 – 2000 the total dioxin emission from the Norwegian magnesium plant has been 0.08 – 0.1 mg I-TEQ/tonne magnesium produced. In the period from the 1950s when the plant was installed to 1976, the annual dioxin discharge load to water was several kilograms. In the period 1976 – 1990 the annual dioxin discharge load was reduced to approximately 500 g I-TEQ. After 1990 when water treatment facilities were installed, the annual discharge load to water has been 1.1 - 2.6 g I-TEQ. In 2000 the total dioxin load emitted from the Norwegian magnesium plant was 1.6 g I-TEQ to air and 1.7 g I-TEQ to water (98). Attention has to be drawn to the fact that only a minority of the dioxin emissions from a non ferro plant are due to point sources. The majority of the dioxin pollutions in the surroundings of a non ferro plant is caused by diffuse emissions, which can be excellently monitored by deposition measurements (see 1.7.3.). Before the sanitation program, dioxin depositions over 100 pg TEQ/m<sup>2</sup>.day were measured in the surroundings of the non ferro plant, after profound measures taken by the plant management, the deposition decreased to 5 pg TEQ/m<sup>2</sup>.day. The dioxin deposition measurement in the surroundings of a steel foundry decreased from 40 to 7 pg TEQ/m<sup>2</sup>.day after a sanitation program which included the careful choice of the type of anthracite used in the process.

### 2.2.3 Power generation and heating

In table 2.2.3 data on annual air emissions for power generation and heating is shown for OSPAR states. The information is very inhomogeneous and difficult to compare. It would also be clearer if the sources 'fossil fuels' and 'biomass fuels' would be entirely separated. There is no data from Norway although some activities must take place.

**Table 2.2.3: Annual air emissions (g I-TEQ) for power generation and heating from OSPAR countries**

UNEP Category 3: Power generation and heating	BE 2004	DK 2002 (46)	FIN 2003 (49)	DE 1995	NL 1991	NO 2004 (145)	SE 2004 (45)	CH 2002 (49)	UK 2003 (47)
Fossil fuel power plants	0.54	0.1-3.2	4.6	14.2	3.7		<4		7
Biomass power plants		0.3-19 (+heating)		2.7	0.8		<10		7
Coal combustion, industrial									48
Landfill, biogas combustion		0.25-10		0.3	0.3				0.4
Wood stoves, virgin wood									
Household heating and cooking (biomass)		0.4-22	13.7		11.2	8	<4	0.3	4.1
Domestic heating (fossil fuels)		0.4-1.3							4.4

In 2003 the annual emissions of dioxins in Denmark from wood stoves burning virgin wood was estimated to 2-4 g I-TEQ (61).

#### 2.2.4 Production of mineral products

In table 2.2.4 the annual emissions of dioxins from production of mineral products in OSPAR states is shown. The reported air emission from Belgium is extremely high and probably not correct

**Table 2.2.4: Annual air emissions of dioxins (g I-TEQ) from production of mineral products in OSPAR countries**

UNEP Category 4: Subcategories	BE 2004	DK 2002 (46)	FIN 2003 (49)	NL 1991	NO 2004 (145)	SE 2004 (45)	CH 2002 (49)	UK 2003 (47)
Cement	0.41	0.15-1.4	0.07		0.08	0.2-0.3	0.003	3.4
Lime	0.15	<0.02	0.15		0.1			0.9
Brick		0.016						
Glass		0.02-0.32	0.03	2.7				
Ceramics								
Asphalt mixing				0.3				1.09

#### 2.2.5 Transportation

The most recent data from OSPAR states on annual air dioxin emissions from transportation are illustrated in table 2.2.5.

**Table 2.2.5: Annual air dioxin emissions (g I-TEQ) from transportation in OSPAR countries**

UNEP Category 5: Transport	BE 2004	DK 2002 (46)	FIN 2003 (49)	FR 1995	DE 1995	NL 1991	NO 2004 (145)	SE 2004 (45)	CH 1995	UK 2003 (47)
4-Stroke engines (cars)	0.41		0.81	1.5			0.2			2.9
2-Stroke engines (mopeds)		0.2			4.7	7.0			0.9	0.09
Diesel engines (trucks)			1.8				0.2			0.54
Heavy oil fired engines (e.g. ships)		1.3-1.5 (incl. trains)	0.9				5	0.2-0.5		8.6 (incl. trains)
Aeroplanes							0.03			0.07

In Sweden and Norway a very detailed estimation concerning dioxin emissions from traffic has been performed, which also included emissions from ships and small aeroplanes (still using leaded fuel), sources which have been ignored by most other studies. Dioxin emissions from shipping using fuels sold in Sweden was estimated to be 0.37-0.85 g TEQ in 2002, and the dioxin emission from traffic in the North Sea and Baltic Sea were estimated to 2.7-6.0 g TEQ in 2002 (45). Emission concentrations of 0.01-0.4 ng TEQ/kWh

are found in one study of ships (150). In times when stationary sources are more and more controlled, transportation becomes a relatively more significant dioxin source.

Not only the type of fuel, but also the engine technology and the possibility for emissions of dust particles are a major source of dioxins in transportation. Ships are large fuel consumers and can have older technology on board, so they pose a direct risk for dioxin contamination of the marine environment.

### 2.2.6 Fires

Natural and accidental fires are sources of increasing relative importance which is shown in Table 2.2.6.

**Table 2.2.6: Annual air emissions (g I-TEQ) from uncontrolled combustion processes (fires) in OSPAR countries**

UNEP Category 6: Uncontrolled combustion	BE 1995	DK 2002 (46)	FIN 2003 (49)	NO 2000	SE 2004 (45)	CH 1995	UK 2003 (47)
Biomass burning (forest, grassland)	2.56	0.03-6.5	1.61			<1	35
Waste burning and accidental fires		0.5-20		3	0.4-65	50	127

Accidental landfill fires occur frequently. In July 2000 such a spontaneous fire, involving 25 000 tonnes of paper and plastic waste, which has been temporarily located on a landfill, happened in Denmark. The fire lasted for about one week, and 75% of the waste was burned. In soot samples taken from surfaces in a residential area close to this landfill in the downwind area low levels of 1-33 ng I-TEQ/m<sup>2</sup> were detected (77).

In a Finnish investigation, levels of 51- 427 pg N-TEQ/m<sup>3</sup> at a landfill fire were determined in the breathing zone five metres from the fire centre (151). The residues contained 100-300 ng N-TEQ/kg material.

In a Belgian study, the impact of the incineration of domestic garbage was investigated. The dioxin deposition increase with 2.5 pg TEQ/m<sup>2</sup>.day on a distance of 20 m. The burning of garden waste led to a rise of 0.8 pg TEQ/m<sup>2</sup>.day (166)

### 2.2.7 Production of chemicals and consumer products

A few recent data on annual dioxin air emission from production of chemicals and consumer products from OSPAR states is shown in table 2.2.7.

**Table 2.2.7: Annual dioxin air emission (g I-TEQ) from production of chemicals and consumer products in OSPAR countries**

UNEP Category 7: Production of chemicals and consumer goods	BE 2004	DK 2002 (46)	FIN 2003 (49)	FR 1995	DE 1995	NL 1991	NO 2004 (145)	SE 2004 (45)	CH 1995	UK 2003 (47)
Pulp and paper mills	0.02		1.16				~ 1	1.2		
Chemical industry	0.01	<0.01	0.08			0.5	0.05			
Petroleum industry	0.06		0.23				~ 1			12.7
Textile plants										
Leather plants										
Chip board production									0.2	

### 2.2.8 Miscellaneous sources

In the Netherlands the concentrations of dioxins in emissions of crematoria were  $<4$  ng I-TEQ/Nm<sup>3</sup>. The emission factor was 4 µg I-TEQ/corpse without and  $<1$  µg I-TEQ/corpse with fabric filter. A recent Danish investigation of a modern crematorium without advanced filters but with pre-warming to 850°C and instant cooling of flue gases determined a much lower emission concentration of 0.06 ng I-TEQ/Nm<sup>3</sup> (at 17% O<sub>2</sub>) corresponding to 0.2 ng I-TEQ/Nm<sup>3</sup> (at 10% O<sub>2</sub>) and an emission factor of 0.25 µg I-TEQ/corpse.

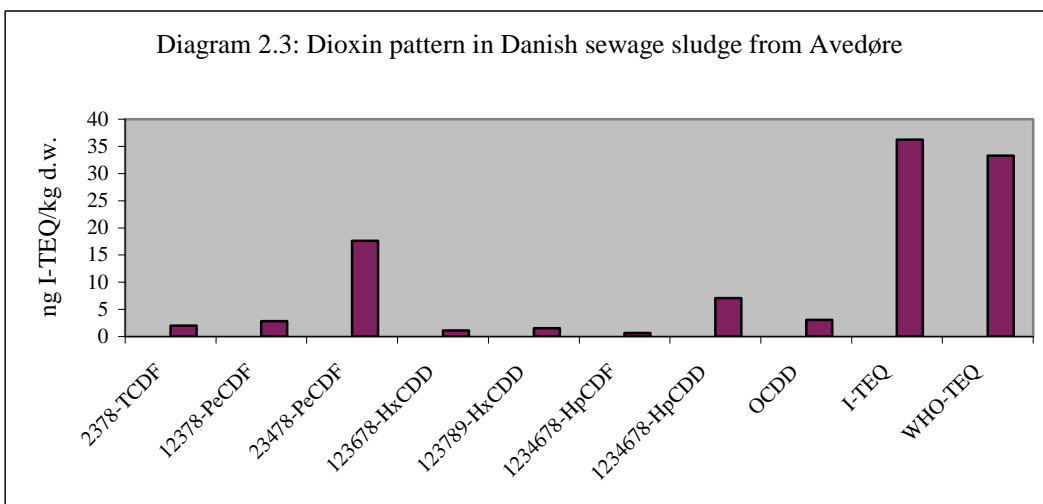
Wood preservation, especially with chlorophenols, has been identified as an important source but only in the Netherlands and Denmark. Dioxins may evaporate or leak from PCP treated wood. Wood preservation is not included as a UNEP subcategory 8 but is added to Table 2.2.8.

**Table 2.2.8: Annual air emissions (g I-TEQ) from miscellaneous sources in OSPAR countries**

UNEP Category 8: Miscellaneous	BE 2003	DK 2002 (46)	FIN 1995	NL 1991	NO 2000	SE 2004 (45)	CH 2002 (49)	UK 2003 (47)
Drying of biomass		<0.04						
Crematoria	0.05	0.04	0.03	0.2	0.11	0.1-0.3	0.3	11
Smoke houses								
Dry cleaning								
Tobacco smoking								
Other sources: Wood preservation (PCP)		0.5-26		25			2.4	

In a Japanese study about 2 ng I-TEQ/m<sup>3</sup> was measured in cigarette smoke (152). The estimated intake is 0.1-1 pg I-TEQ cigarette based on Japanese, Swedish and German studies.

Sewage sludge from Denmark, Germany, Sweden and the UK contains 10-50 ng I-TEQ/kg dry weight, and maximum levels have been measured at around 200 ng I-TEQ/kg dry weight. In Germany, a sewage sludge limit value has been set at 100 ng I-TEQ/kg dry weight. Sewage sludge from Belgium contains 20-26 pg WHO-TEQ/g dw. Dredgings contained 24 pg WHO-TEQ/g dw. (164) In Diagram 2.3 the dioxin pattern in a Danish sewage sludge sample from Avedøre treatment plant near Copenhagen is shown (153).



Only the most important congeners are included. Here, the total level expressed as WHO-TEQ was lower than I-TEQ.

There are only available data on annual dioxin emission to water in a few OSPAR countries as shown in table 2.2.9. For Belgium, no later data are available.

**Table 2.2.9: Annual dioxin emissions (g I-TEQ) to waters from disposal practices**

UNEP Category 9: Disposal	BE 1995	DK 1999	SE 1995	UK 1997
Landfill leachate		<0.05		
Sewage/sewage treatment	9.74	0.3-1.4	0.11	0.41-1.6
Open water dumping				
Waste oil disposal				0.28-1.2

No available specific information about hot spots in OSPAR states was found.

### 2.2.9 Total emissions in OSPAR Countries

A compilation of the total air emissions of dioxins from OSPAR states based on available recent inventory studies is shown in Table 2.2.11.

**Table 2.2.11: Total annual dioxin air emissions (gram I-TEQ) with different reference year from sources in various OSPAR countries**

Country Year	Typical values or ranges in g TEQ/year							UNEP 1995 (30)
	1985	1990	1991	1992	1993	1994	1995	
Belgium (33)	868 <sup>#</sup>	892			706		662	661
Denmark (32, 34-36)				94			40	39
Finland (30-32)		35.4*	34.8*	33.1*	25;34.7*	41.5*	56-74; 40.7*	98-198
France (30-32)		900; 2206 <sup>#</sup>	2268 <sup>#</sup>		621; 2312 <sup>#</sup>	2363 <sup>#</sup>	2107 <sup>#</sup>	873
Germany (30, 37) <sup>§</sup>		1210; 1196 <sup>#*</sup>			600	333	307 <sup>#*</sup>	334
Iceland*		10.1	10.0	9.7	8.8		7.0	
Ireland (32)							24-40	
Luxembourg (31)					30		27-54	
Netherlands (39)	874 <sup>#</sup>		484					486
Norway (30-32,44)	593 <sup>#</sup>	130	98	96	45;95	94	34-90;70	9
Portugal (32)							90-136	
Spain (31-32)					134		131-388	
Sweden (32,40)	93 <sup>#</sup>	31-115			21-88		23-30; 28-108	22
Switzerland (41)	439 <sup>#</sup>	242					180	181
UK (32, 42, 43)		1092	1074	1050	1007	905	560-1100; 778; 819*	569

<sup>§</sup> Data from Germany respectively for 89/90 and 94/95. <sup>#</sup> Data reported to Fifth North Sea Conference. \* Data submitted to OSPAR for the purpose of this report. All Icelandic data are national data also reported to EMEP.

**Table 2.2.11: Continued.**

Country Year	Typical values or ranges in g TEQ/year									
	1996	1997	1998	1999	2000 (or forecast)	2001	2002	2003	2004	
Belgium (33)					185 <sup>#</sup>					
Denmark (32, 34-36,46)				19-170; 94 <sup>#</sup>	45-72		87			
Finland (30-32,49)	39.8*	39.1*	39.5*	41.1*	64-82		32	32		
France (30-32)	983; 1865 <sup>#</sup>	435; 1253 <sup>#</sup>	350; 836 <sup>#</sup>	227; 558 <sup>#</sup>	200					
Germany (30,37) <sup>§</sup>					70; 197-472					
Iceland*	6.4	6.2	5.2	4.4	4.0	3.6	3.5	2.9		
Ireland (32)					25-39					
Luxembourg (31)					8-12					
Netherlands (39, 49, 154)				42 <sup>#</sup>	58; 31	30	29;41	40		
Norway (30-32,44)	50	41	22;34	19 <sup>#</sup> ;39	34	33	32	29	33	
Portugal (32)		8.5-31			82-123					
Spain (31-32) Tarragona area (48)				2.24	117-327					
Sweden (32,40,45)				33 <sup>#</sup>	26-98				<33-105	
Switzerland (41,49)					72; 133 <sup>#</sup>					
UK (32,42,43,47)	219-663; 532	325	361*	345*	243-649			323		

Not all OSPAR states were able to submit data, and the information is probably not quite up-to-date, because much information is 5-10 years old. Moreover, for some countries additional datasets from various years are included. Some data are based on actual measurements; others are only a best estimate. Some of the data in the European inventory have been taken from CORINAIR reports.

Concerning emissions to other environmental compartments than air the data is scarcer. In table 2.2.12 data on direct releases to the aquatic environment, soil and residues are presented.

**Table 2.2.12: Total dioxin emissions to water, soil and residues in some OSPAR states:**

Country	Gram I-TEQ/year to water		Gram I-TEQ/year to soil/land		Gram I-TEQ/year to residue/landfill	
	Best estimate	Range	Best estimate	Range	Best estimate	Range
Belgium (33)	3.77					
Denmark (36)		0.3-1.4		1.3-54		38-416
Netherlands (39)	3				1055	
Sweden (40)		1.6-5.1				35-52
Switzerland (41)	6		9		110	
UK (155)		1.0-30				1500-12000*

\*Includes discharges to soils.

The estimated global dioxin emissions to air and accumulated emission data from different groups of countries are shown in Table 2.2.13 (Data from UNEP 1999 (30)).

**Table 2.2.13: Estimated dioxin air emission data from aggregated mixtures of countries**

	Gram I-TEQ/year	Number of countries
Global emission annually 1995	50 000	
Known inventories, UNEP 1995	10 500	15
38 European countries 1990	11 300	
EU 1990	6 250	15
EU 1995	5 750	15
European Inventory 1995	3 685-6 470	17
European Inventory 2000	2 435-4 660	17
European Inventory 2005 (projection)	1 959-3 834	
OSPAR countries 1990	5 840	15
HELCOM 1990	3 230	9
Central and Eastern Europe 1990	5 070	19

## 2.3 The extent of the problem

It was already mentioned that the toxicity of dioxins is mediated through an interaction with the Ah receptor. The latter is a highly conserved protein throughout evolution. While the exact role of the receptor is unclear, it is assumed that it plays a critical role in numerous biological systems. Most species respond similar to dioxin exposure and humans appear to have similar sensitivities as animals (21). Because of the consistency of the observed effects and the evolutionary conservation of the AhR, potential risks apply to humans and animal species.

For the marine environment, top-predators, such as fish consuming birds and marine mammals, will be the most likely affected species. The WHO recommends a tolerable daily intake (TDI) of 1-4 pg WHO-TEQ/kg body weight for dioxins and dioxin-like PCBs. This recommendation was adopted by the European Scientific Committee on Food (SCF) and transferred into a tolerable weekly intake (t-TWI) of 14 pg TEQ/kg body weight. A considerable part of the European population has a current intake which is higher than this t-TWI. In the Netherlands the daily intake is 1.8 pg/kg body weight, of which 0.25 pg/kg body weight (14%) is due to seafood consumption, with the remainder due to other food. This implies that by simply setting tolerance levels for dioxins and dioxin-like PCBs in seafood a substantial reduction of the dioxin intake by the population of the Netherlands will not be achieved. Even a total ban on seafood consumption would not reduce the t-TWI to 7 pg TEQ/kg body weight corresponding to the lower end of the WHO recommendation.<sup>7</sup> In the Netherlands, a dioxin tolerance level of 8 ng WHO-TEQ/kg was set solely for eel (156). If the TDI values were applied to fish consuming marine organisms, levels in fish should decrease substantially. For example, the daily intake of dioxins should be limited to 40 or 160 pg TEQ for a harbour porpoise with a weight of 40 kg, depending whether the highest or lowest WHO TDI is considered. For the porpoise consuming an average fish quantity of 3 kg (157), dioxin levels in fish should be less than 13-53 pg/kg. Even though the levels in fish are currently below 1 ng TEQ/kg, a 10 to 100-fold reduction of these levels would be necessary in order to reach the recommended TDI ranges.

## 3. Desired reduction

The 1990 Hague Declaration adopted by the 3<sup>rd</sup> North Sea Ministerial Conference sets, *inter alia*, for chlorinated dioxins a reduction target of 70% for the total inputs. However, at the North Sea Conference in 1995 the Ministers strengthened this target into a 'cessation target within one generation', which was also the basis for the objective of the OSPAR Strategy with regard to Hazardous Substances.

PCDDs and PCDFs are on the OSPAR List of Chemicals for Priority action. The OSPAR objective with regard to hazardous substances on this list is to prevent pollution of the maritime area by continuing to reduce discharges, emissions and losses of hazardous substances, with the ultimate aim of achieving concentrations in the marine environment near background values for naturally occurring substances and close to zero for man-made synthetic substances. Every endeavour has to be made to move towards the target of cessation of discharges, emissions and losses of hazardous substances by the year 2020.

<sup>7</sup> The WHO recommendation has been superseded by the EC Scientific Committee for Food recommendation of 14 pg/kg bw per week and the Joint FAO/WHO Expert Committee on Food Additives recommendation of 70 pg/kg bw per month.



## 4. Identification of possible measures

In the following agreed national and international measures are compiled. Further, possible new programmes are indicated.

### 4.1 International agreements

#### 4.1.1 UN ECE Protocol on Persistent Organic Pollutants (POPs)

The UN/ECE Convention on Long-Range Transboundary Air Pollution has developed a Protocol on persistent Organic Pollutants (POPs), which was signed in Aarhus, 24 June 1998. This protocol includes dioxins and furans among substances to which mandatory control measures apply.<sup>8</sup> Mandatory Emission Limit Values (ELVs) were established for dioxin emissions from waste incineration, which was listed as the major source. Further, the use of best available technology (BAT) to reduce emissions was generally approved. The ELVs are 0.1 ng TEQ/m<sup>3</sup> for municipal waste, 0.2 ng TEQ/m<sup>3</sup> for hazardous waste and 0.5 ng TEQ/m<sup>3</sup> for medical waste.

#### 4.1.2 UNEP POPs Convention

The UNEP Convention on Persistent Organic Pollutants (POPs) adopted in Stockholm, 22 May 2001, and signed by 91 countries and the European Commission requires measures for reducing or preventing releases of dioxins to the environment. One of the requirements is to develop an action plan designed to identify, characterise and address the release of dioxins, and develop and maintain (comparable) national source inventories and release estimates (see chapter 1.4.1). The action plan shall include the following elements:

- an evaluation of current and projected releases;
- an evaluation of the efficacy of the laws and policies related to the management of the releases;
- strategies to meet the obligations;
- steps to promote education and training;
- review and reporting every five years;
- a schedule for implementation of the action plan.

Further, it is required to:

- promote the application of available, feasible and practical measures for release reduction and source elimination;
- promote the development and use of substitute products and processes to prevent formation and release of dioxins;
- promote and require use of best available techniques and best environmental practices for new and existing sources.

The Stockholm Convention entered into force 17 May 2004, and many countries and the European Commission will develop implementation plans during 2006. Until September 2006, 33 countries have submitted implementation plans; of these were seven EU countries (Czech Republic, Denmark, Finland, Germany, Latvia, Netherlands and Sweden) and two more OSPAR Countries (Norway and Switzerland).

#### 4.1.3 North Sea Conferences

The *North Sea Conference* has no formal instruments for the implementation of the reduction target. However, a list of possible measures was included in the 1995 Esbjerg declaration.

#### 4.1.4 The Barcelona Convention

The revised Protocol of the Barcelona Convention for the Protection of the Mediterranean Sea against Pollution from Land-based sources and Activities includes dioxins in the list of substances to be controlled.

<sup>8</sup> UN/ECE EB.AIR/1998/1+2.

#### **4.1.5 The Basel Convention**

The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal regulates the movements and provides obligations to its Parties to ensure that such wastes are managed and disposed of in an environmentally sound manner. PCBs and dioxins are classified as hazardous wastes.

#### **4.1.6 The Helsinki Convention (HELCOM)**

The Convention for the Protection of the Marine Environment of the Baltic Sea Area addresses the ban on the production and marketing of articles and equipment containing PCBs/PCTs in its HELCOM Recommendation 6.1 of 1987. This Recommendation is complemented by a provision banning all uses except in existing closed systems until the end of their service life. HELCOM has produced a "Guidance Document" on dioxins and in 2004 a short illustrative report on dioxins was published as "Environmental Focal Point Information".

#### **4.1.7 FAO/WHO Codex Alimentarius Commission**

In 2000 at the 32th Session, the Codex Committee on Food Additives and Contaminants began its work on a proposed "Code of Practice for source directed measures to reduce dioxin and dioxin-like PCB contamination of foods". The draft was promoted to stage 8 at the last 38<sup>th</sup> Session in The Hague, The Netherlands, 24-28 April 2006.

### **4.2 EU Regulations**

#### **4.2.1 Community Strategy for Dioxins, Furans and PCBs**

The European Commission has 24 October 2001 published a Communication – COM (2001) 593 final - on a strategy to reduce the presence of dioxins, furans and PCBs in the environment, food and fodder. This strategy for dioxins, furans and PCBs consists of two parts. The first part identifies actions in the short term (5 years) covering hazard identification, risk assessment, risk management, research, communication to the public and cooperation with third countries and international organisations. It further identifies long term actions (10 years) covering data collection, monitoring and surveillance. The implementation of the first part will provide a comprehensive picture of the environmental dioxin/PCB problem and a good understanding of existing trends, which will allow further policy making and evaluation. The second part proposes a strategy consisting of three pillars: the "establishment of maximum limits" in food and fodder, action levels that acts as tools for the "early warning" of higher than desirable levels of dioxins in food or fodder, and "target levels" in food and fodder. These targets should be achieved in order to reduce the current exposure levels of a large part of the European population to lower levels than the tolerable intake levels established by the Scientific Committee for Food. The implementation of this strategy should apply the precautionary principle with a view to take action without unnecessary delay. Council conclusions were established in December 2001. These conclusions set priorities for the work of the European Commission to be carried out in future.

On 13 April 2004 a report on the progress of the Dioxin Strategy was adopted - COM (2004) 240. It summarises the main work that has been done by the Commission during the first two years since the adoption of the Strategy. The activities include projects targeted on the New Member States, work on integrated environment and health information focussed on the Baltic Sea, work on best available techniques, research, limit values for dioxins in feed and food and work on screening methods (deposition measurements).

#### **4.2.2 Regulation no. 850/2004 of the European Parliament and Council of 29 April 2004 on persistent organic pollutants and amending Directive 79/117/EC. The European Community POP Implementation Plan**

This Regulation aims to align the Community legislation with the requirements of the two internationally binding instruments on POPs, the Protocol to the regional UNECE Convention on Long-Range Transboundary Air Pollution and the global Stockholm Convention. At the same time, it goes further than the international obligations by emphasising the aim to eliminate the production and use of the internationally recognised POPs.

The most important development right now is the elaboration of the POP Regulation Community Implementation Plan. As regards release reduction for unintentionally produced POPs (dioxins, PCBs, PAH, HCB) DG Environment has launched a study to identify the most relevant measures to be taken at EU level. A draft final report is expected any day (June 2006). The findings of this study will form the basis for the measures to be proposed for the Implementation Plan which will be formulated during autumn this

year. OSPAR is invited to take part in this work by commenting of the suggested measures in order to ensure coherence.

#### **4.2.3 Framework Directive on ambient air quality assessment and management (96/62/EC)**

The Commission plans to set up a daughter Directive on dioxin deposition to this Council Directive.

#### **4.2.4 Council Directive 96/61/EC concerning integrated pollution prevention and control (IPPC)**

The IPPC Directive covers many relevant industrial sectors that generate dioxins, and BAT Reference Documents (BREFs) address dioxins explicitly, giving clear indications on achievable emission values. The Directive is an “integrated approach” (i.e. addressing all environmental media– air, water, soil simultaneously) to industrial emission control for dioxin emissions. All installations covered by Annex I of the Directive, including installations with dioxin emission potential are required to obtain a permit from the authorities in the EU Member States. The permits must be based on the concept of best available techniques (BAT) and must include emission limit values (ELVs) for certain pollutants such as dioxins. The Directive provides for the set-up of a European Pollutant Emission Register, which is a monitoring and harmonisation mechanism designed to collate and publish every three years an inventory of the principal industrial emissions, including dioxin emissions to the air and their sources. Existing installations have to comply by October 2007. The Directive includes an information exchange on PCDD/PCDF prevention and abatement techniques, on associated emission values in the BREFs and on the development of emission values for PCDD/PCDFs.

#### **4.2.5 The Directives on releases to water**

Council Directive 76/464/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community establishes the framework for laying down emission limit values and environmental quality standards at EU level for certain categories of substances, including dioxins and PCBs. The Water Framework Directive 2000/60/EC (158) integrated the provisions under 76/464/EEC and can provide for the progressive reduction or cessation of discharges and losses of pollutants to water. However, dioxins and furans are not included in the Water Framework Directive list of priority substances.

#### **4.2.6 The Directives on wastes**

In 1989, for the first time the EU adopted legislation (159) to reduce dioxin emissions from municipal waste incineration by setting up so-called operational conditions, leading to a significant reduction of dioxin emissions. In response to the target set by the fifth Environment Action Programme (EAP), Council Directive 94/67/EC on the incineration of hazardous waste has laid down for the first time an emission limit value (ELV) at Community level. The Directive 2000/76/EC on the incineration of waste sets an air emission limit value of 0.1 ng I-TEQ/Nm<sup>3</sup> for all waste incinerators and for stationary sources with co-incineration of waste, for instance cement kilns. This Directive also sets a discharge limit value of 0.5 ng I-TEQ/l or 150 ng I-TEQ/tonne of waste. When fully implemented, the Directive will reduce dioxin emissions within the Community from an annual 2400 grams in 1995 to only 10 grams in 2005.

This new Directive, which sets an ELV for all waste incinerators, aims to reduce as far as possible negative effects on the environment caused by the incineration and co-incineration of waste and also addresses the incineration of non-hazardous waste, which was once the largest source of emissions of dioxins into the atmosphere. The dominant source of dioxins in the EU has traditionally been uncontrolled waste incineration.

#### 4.2.7 The Seveso Directives

The Seveso Directives are important for the protection of communities in the neighbourhood of installations with a potential risk and seek to avoid serious accidents such as the Seveso accident in 1976. Directive 96/82/EC, superseding Directive 82/501/EEC, aims to prevent major accidents and hazards involving dangerous substances such as dioxins. Secondly, because chemical accidents still continue to happen, it aims to limit the consequences of such accidents. They include the provision that sites qualify as possible major accident sites, if the total dioxin stored at this site reaches 1 kg.

#### 4.2.8 Dioxin in feedstuff

A Council Directive 2001/102/EC amending the 1999/29/EC Directive on the undesirable substances and products in animal nutrition has been adopted 27 November 2001.

**Table 4.2.1: EU limit values for dioxin in fodder**

Fodder	Maximum content relative to a feeding stuff with a moisture content of 12%
All fodder of plant origin including vegetable oils and by-products	0.75 ng WHO-PCDD/F-TEQ/kg
Minerals	1.0 ng WHO-PCDD/F-TEQ/kg
Animal fat, including milk fat and egg fat	2.0 ng WHO-PCDD/F-TEQ/kg
Other land animal products and eggs and egg products	0.75 ng WHO-PCDD/F-TEQ/kg
Fish oil	6 ng WHO-PCDD/F-TEQ/kg
Fish, other aquatic animals, their products and by-products with the exception of fish oil	1.25 ng WHO-PCDD/F-TEQ/kg
Compound fodder, with the exception of fodder for fur animals and fodder for fish	0.75 ng WHO-PCDD/F-TEQ/kg
Fodder for fish	2.25 ng WHO-PCDD/F-TEQ/kg

It should be noted that fresh fish which is directly delivered and used without intermediate processing into fodder is exempted from these provisions.

A Commission Directive 2002/70/EU of 26 July 2002 define sampling and analysing methods for official control of dioxin and dioxin-like PCBs in feedstuffs.

#### 4.2.9 Dioxin in foodstuffs

Commission Regulation EC No. 466/2001 and later amendments are setting maximum levels for certain contaminants in foodstuffs. The Council Regulation EC No. 2375/2001 established limit values for PCDD/Fs in various foodstuffs. A recent amendment to this is Commission Regulation EC No. 199/2006 of 3<sup>rd</sup> February 2006 which is setting limits for both PCDD/Fs and dioxin-like PCBs in foodstuffs.

**Table 4.2.2: EU limits values for food, 2006.**

Food	Maximum levels Sum of dioxins and furans (WHO- <sub>PCDD/F</sub> -TEQ)	Maximum levels Sum of dioxins, furans and dioxin-like PCBs (WHO-TEQ)
<b>Meat and meat products</b>		
- of ruminants (bovine animals, sheep)	3.0 pg/g fat	<b>4.5 pg/g fat</b>
- of poultry and farmed game	2.0 pg/g fat	<b>4.0 pg/g fat</b>
- of pigs	1.0 pg/g fat	<b>1.5 pg/g fat</b>
<b>Liver of terrestrial animals and derived products thereof</b>	6.0 pg/g fat	<b>12.0 pg/g fat</b>
<b>Muscle meat of fish and fishery products and products thereof with the exception of eel</b>	4.0 pg/g fresh weight	<b>8.0 pg/g fresh weight</b>
<b>Muscle meat of eel (<i>Anguilla anguilla</i>)</b>	4.0 pg/g fresh weight	<b>12.0 pg/g fresh weight</b>
<b>Milk and milk products, including butter fat</b>	<b>3.0 pg/g fat</b>	<b>6.0 pg/g fat</b>

Commission Directive 2002/69/EU of 26 July 2002 defines sampling and analysing methods for official control of dioxin and dioxin-like PCBs in foodstuffs.

#### **4.2.10 Other “Chemicals” Directives**

##### **Restrictions on marketing and use of dangerous substances**

In 1985, the use as a raw material and chemical intermediates of PCBs and polychlorinated terphenyls (PCTs) has been banned by Council Directive 85/467/EEC (6<sup>th</sup> amendment to Directive 76/769/EEC on the approximation of the laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations).

##### **Shipment and disposal of PCB-containing waste**

Although PCBs and dioxins have been classified as hazardous waste in Council Directive 91/689/EEC on hazardous waste, the European Commission has recognised that further legislation on the disposal of PCB-containing waste would be necessary. Council Directive 75/439/EEC on the disposal of waste oils set a maximum limit of 50 ppm for the PCB content of regenerated oil or oil used as fuel. Council Regulation (EEC) No 259/93 on the supervision and control of shipments of waste within, into and out of the European Community sets strict control procedures for the shipment of PCB-containing waste so as to avoid their illegal dumping. The disposal of PCBs and PCTs has been regulated by Council Directive 96/59/EC aiming at complete disposal of PCBs and equipment containing PCBs as soon as possible, and for large equipment before the end of 2010. This Directive sets the requirements for an environmentally sound disposal of PCBs. EU Member States have to make an inventory of relevant equipment containing PCBs within 3 years of its adoption and submit a detailed plan for the disposal of relevant PCB wastes and equipment. The Directive further outlines provisions for the collection and disposal of small equipment (small electrical devices very often present in household appliances manufactured before the ban on production of PCBs) which are not included in the inventory. The proposal for a Directive on Waste from Electric and Electronic Equipment, which is now being discussed by Council and the European Parliament, will certainly contribute to the separate collection and environmentally sound disposal of electrical equipment containing PCBs, as it contains an explicit obligation for the separation of the hazardous components of electric and electronic equipment before any subsequent treatment is applied. Commission Directive 1999/31/EC on the landfill of waste has resulted in a significant change in the volume and nature of waste accepted at landfill sites. It also improved the design and operating standards, as well as in the after-care phases of new and existing landfills. Therefore, this Directive will contribute to a significant decrease in the releases of PCBs from landfills.

### **4.3 National regulations**

#### **4.3.1 Denmark**

The new Danish Air Pollution Guideline of 2001 implements the EU emission limit value of 0.1 ng I-TEQ/m<sup>3</sup> normalised to 11% O<sub>2</sub> for waste incineration. In addition, industries with an annual mass flow of dioxins > 0.01 gram shall meet the emission limit value. The emission guideline value is 0.1 ng/m<sup>3</sup> but may in certain cases be 0.2 ng/m<sup>3</sup> (160).

The contents of dioxin and dioxin-like PCBs in large salmons and herring from the Baltic Sea, east of the island of Bornholm, often exceed the new EU limit values. Thus in 2004 a ban was issued on fishing and sale of herrings and salmons above 4.4 kg fresh weight. Later in accordance with the Statutory Order no. 851 of 15 September 2005, sale of large salmons was again allowed, if excess fat was removed according to a process specified by the Veterinary and Food Administration.

#### **4.3.2 Germany**

The Federal Emissions Control Act (Bundes-Immissionsschutzgesetz, BImSchG) (38) includes the following:

- Technical Instructions on Air Quality (TA-Luft) of 1986 define a general law to minimise dioxin emissions;
- in the maximal allowable concentration list (MAK Liste), 2,3,7,8-TCDD is unambiguously classified as a carcinogen;
- in the Ordinance of 1988 on small firing installations, only certain fuels not coated with halogenated organic compounds are permitted;

- in the Ordinance of 1990 on combustion plants for waste, an emission value of 0.1 ng TEQ/m<sup>3</sup> was introduced;
- in the Ordinance of 1992/2000, the use of chlorinated and brominated compounds as additives in fuels was prohibited;
- the requirements of the “Technical Instructions on Air Quality Control” of 2002 must be observed when licensing installations under the Federal Immission Control Act. This specifies as a minimum requirement that the mass concentration of PCDDs/PCDFs in atmospheric emissions also be 0.1 ng/m<sup>3</sup> and the mass flow 0.25 µg/h.
- the Ordinance of 2003 specifies requirements relating to the construction, type, and operation of waste incinerators or co-incinerators. It stipulates that PCDD/PCDF concentrations in the exhaust stream of incinerators may not exceed an emissions limit value of 0.1 ng TEQ/m<sup>3</sup>. Emission limit values for incinerators burning solid municipal waste are also 0.1 ng TEQ/m<sup>3</sup>.
- in the Ordinance of 2004, sets the limit value for PCDDs/PCDFs at 0.1 ng TEQ/m<sup>3</sup> for large combustion plant and gas turbines.

#### **4.3.3 Switzerland**

The Ordinance on risk reduction related to the use of certain particularly dangerous substances, preparations and articles (ORRChem SR 814.81) in force since 1 August 2005 is limiting PCDDs/Fs in fertilizers to 20 ng I-TEQ/kg dry substances.

#### **4.3.4 France**

The regulation on the determination of combustion conditions for household waste incinerators of 25 January 1991 stipulates technical conditions on waste combustion. No emission threshold values were defined.

The regulation on waste incineration of 10 October 1996 defines a threshold value for dioxins of 0.1 ng/m<sup>3</sup> for the incineration of special industrial waste.

The regulation on waste incineration of 20 September 2002 extends the previously defined threshold value to all incinerators of waste (0.1 ng/m<sup>3</sup>).

#### **4.3.5 Belgium**

Since 13 February 2004, in Flanders an emission threshold for waste incinerators (including crematoria and large wood incinerators) is set at 0.1 ng I-TEQ/Nm<sup>3</sup>. For refineries, limit values between 0.1 ng I-TEQ/Nm<sup>3</sup> and 1.0 ng I-TEQ/Nm<sup>3</sup> are applicable. For metal industries, limit values between 0.1 ng I-TEQ/Nm<sup>3</sup> and 2.5 ng I-TEQ/Nm<sup>3</sup> are applicable. Small wood incinerators have a limit value of 0.4 ng I-TEQ/Nm<sup>3</sup>.

## **5. Choice for action**

On 12 December 2001, the EU Council of Ministers adopted conclusions on the “Communication from the Commission to the Council, the European Parliament and the Economic and Social Committee on a strategy for dioxins, furans and polychlorinated biphenyls”. Among other matters, these conclusions:

- underline the need to implement and enforce rigorously the existing legislation;
- invite the EU Commission to come up with new measures based on the precautionary principle;
- ask the EU Commission to make the calendar of the strategy compatible with the short term strategy for the reduction of Dioxins, PCBs and Furans in food and fodder;
- invite the EU Commission to come up with an integrated norm for toxicity (taking account of the recent WHO TEF definition);
- ask the EU Commission to propose EU wide emission limit values in accordance with art. 18 of the IPPC Directive whenever a need for Community limits is identified;
- recognise the need to promote, and if needed replace, certain materials, products and processes identified as non-intentional sources of dioxin and furans emission;
- note the need to address smaller industrial sources;
- draw the attention on the rising importance of non-industrial sources of dioxins.

Since these conclusions cover much of the relevant ground,

- the OSPAR lead countries for dioxins and furans should keep under review the implementation of these EC actions and, where appropriate, bring forward to OSPAR any proposals necessary for action to achieve the goals of the OSPAR Strategy with regard to the Hazardous Substances which will not be covered by the EC work.

In the short term, areas where OSPAR might be able to make a valuable contribution are the industrial sources not covered by Integrated Pollution Prevention and Control systems, and non-industrial sources. The latter, in particular, are not regulated or subject only to limited controls. In particular, account could be taken of the needs to control contaminated waste and to promote, and where appropriate, require the substitution of materials, products and processes leading to unintentional formation of dioxins and furans.

- The OSPAR lead countries for dioxins and furans should review what action might be appropriate in such areas and bring forward a focused consideration of the sources mentioned above, their likely impact on the marine environment and proposals for any relevant, practicable and cost-effective measures that could be proposed to eliminate/abate these sources as far as possible.
- Preliminary data on dioxin emissions from ships in this report indicate that this emission source warrants action by OSPAR, taking into account work by other competent international organisations, to obtain more precise estimates of the dioxin emissions from shipping in the North-East Atlantic and its contribution to inputs to the maritime area. This work can inform considerations of any further actions to address this source, including, when appropriate, that OSPAR addresses a communication to the IMO

To ensure that the information in this background document and the conclusions reached by OSPAR are formally communicated to the European Commission,

- OSPAR should communicate this Background Document to the European Commission.

To ensure that the information in this background document can be considered in the context of other international agreements, which deal with hazardous substances and to which Contracting Parties are associated,

- OSPAR should send copies of this background document to the appropriate bodies dealing with those agreements and invite Contracting Parties who are common parties to OSPAR and those other agreements to promote action to take account of this background document by those other international bodies in a consistent manner.

To ensure that information from other international agreements such as the Stockholm Convention is taken into account in the further policy making with respect to dioxins and furans.

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## Appendix 1: Monitoring Strategy for Chlorinated Dibenzo-*p*-dioxins and Chlorinated Dibenzofurans (“Dioxins”)

As part of the Joint Assessment and Monitoring Programme (*reference number 2003-22*), OSPAR 2005 adopted a revised Agreement on Monitoring Strategies for OSPAR Chemicals for Priority Action (*reference number 2004-14*) to implement the following monitoring for tracking progress towards the objectives of the OSPAR Hazardous Substances Strategy (*reference number 2003-21*) with regard to dioxins. The monitoring strategy for dioxins will be updated as and when necessary, and redirected in the light of subsequent experience.

Dioxins have no commercial uses besides as laboratory standards but occur as contaminants in various commercial products. Dioxins are mainly formed as unintended by-products in heating and combustion processes involving organic matter, chlorine and metal catalysts. Dioxins are emitted either from diffuse sources and point sources via stack gasses or wastewater pipes. The diffuse sources become more and more important.

There are several international agreements on dioxins (UN ECE protocol on POPs, UNEP POPs Convention). There are also several relevant EU measures, including regulations of contaminant levels in food and feed, but dioxins are not on the EU Water Framework Directive list of priority substances. OSPAR should follow progress in the implementation of international measures as part of the monitoring strategy for dioxins.

The direct releases of dioxins into the water environment by rivers and sewage water have diminished during the last decade. Since dioxins are insoluble in water monitoring of the extremely low sea water levels is not appropriate. The source-oriented approach is preferable for dioxins, because most sources nowadays are airborne.

The majority of dioxin sources are already specified in the EUROSTAT nomenclature for sources of emissions (NOSE) used by the EU IPPC Directive, CORINAIR, UN-ECE annual reporting (EMEP) and the European Dioxin Inventory I-II. However, for dioxin emission reporting it would be appropriate in the future to use the newer global UNEP toolbox developed specifically for creation of emission inventories for dioxin in connection with the UNEP POP Convention.<sup>9</sup>

It should be the main objective to develop a general scheme that can enable the emissions of dioxins from various OSPAR countries to be quantified and reported annually to OSPAR in a transparent and harmonised way in order to allow reliable comparisons and trend analysis as a basis for continuing source reduction. The inventory should be based on measurements and/or on emission factors presented by the UNEP dioxin toolbox.

Marine sediments are major sinks and aquatic reservoir for anthropogenic dioxins, and the residence times there are hundreds of years. Without any doubt sediments is a matrix of choice for spatial and temporal monitoring of dioxin in the marine coastal environment. Analysis of dioxin in sediments cores can be used to illustrate trends lasting decades back in history and discover the natural background levels. Dioxin analysis of surface sediments reflects a recent load, and dioxin analysis of coastal and estuarine sediments can reveal present or recent industrial point sources or the load from cities and rivers.

The other important matrix is biota. The highest dioxin levels are found in fatty tissues and livers; therefore, organisms with a high tissue content of fat are potentially most contaminated. The highest levels of dioxin in fish muscle are found in fatty fish such as herring and salmon. National food agencies in most OSPAR countries are already analysing, or are planning to analyse, dioxins in commercial fish and fish products e.g. in order to control the compliance with the new EU fresh weight limit value for dioxin. Herring is one of the most frequently used fish species for monitoring of dioxins in the marine environment. It is therefore recommended that dioxin content in fish and shellfish is monitored as part of the monitoring strategy.

Since dioxins are expected to be found in sediments and biota and national monitoring is ongoing, dioxins should be considered included in the Coordinated Environmental Monitoring Programme (CEMP). If so, there is need to establish background concentrations.

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<sup>9</sup> UNEP Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases. Edition 2.1. Geneva: UNEP Chemicals, December 2005.

<b>CHLORINATED DIBENZO-p-DIOXINS AND CHLORINATED DIBENZOFURANS (“DIOXINS”) MONITORING STRATEGY</b>	
<b>Implementation of actions and measures</b>	<ul style="list-style-type: none"> <li>Examination of progress in the implementation of regulations on emission and/or discharge which have been agreed, or are endorsed, by the Background Document</li> </ul>
<b>Emissions to air</b>	<ul style="list-style-type: none"> <li>Examination and assessment of trends in emissions to air as reported annually by Contracting Parties to the UNECE/EMEP database in the context of LRTAP Convention and, for IPPC sources, to EPER</li> <li>The national inventories of dioxin sources and emissions should be updated annually applying the UNEP toolbox.</li> <li>Develop an assessment model for the emissions of ships.</li> </ul>
<b>Discharges and losses to water</b>	<ul style="list-style-type: none"> <li>Examination and assessment of trends in discharges to water from IPPC sources in data reported annually by Contracting Parties to EPER.</li> </ul>
<b>Production/use/sales/figures</b>	<ul style="list-style-type: none"> <li>Not relevant</li> </ul>
<b>Atmospheric inputs</b>	<ul style="list-style-type: none"> <li>currently no monitoring in OSPAR</li> </ul>
<b>Riverine inputs</b>	<ul style="list-style-type: none"> <li>currently no monitoring in OSPAR</li> </ul>
<b>Inputs from the offshore industry</b>	<ul style="list-style-type: none"> <li>currently no monitoring in OSPAR</li> </ul>
<b>Maritime area:</b>	
<b>Dredged Materials</b>	<ul style="list-style-type: none"> <li>currently no monitoring in OSPAR</li> </ul>
<b>Concentrations in sediments</b>	<ul style="list-style-type: none"> <li>In the light of the assessment of CEMP data to be carried out in 2004/05, OSPAR 2005 will arrange for reviews of whether the CEMP should include monitoring for dioxins</li> <li>Establish background concentrations</li> <li>Compile and assess existing data on sediment concentrations</li> <li>A one-off hot-spots survey of concentrations of dioxins and furans in coastal sediments</li> </ul>
<b>Concentrations in water</b>	<ul style="list-style-type: none"> <li>not relevant</li> </ul>
<b>Concentrations in biota</b>	<ul style="list-style-type: none"> <li>OSPAR Contracting Parties are recommended to monitor in a coordinated way the dioxin levels in fish and shellfish</li> <li>Compile and assess existing data on biota other than those used for food safety control</li> <li>An attempt will be made to develop methods whereby the level and extent of contamination of marine biota by dioxins and furans can be estimated on the basis of monitoring of fish and shellfish carried out by food authorities to protect public health.</li> </ul>