ENVIRONMENTAL CONCENTRATIONS AND ECOTOXICOLOGICAL EFFECTS OF PCDDs, PCDFs AND RELATED COMPOUNDS

Rappe, C.
Institute of Environmental Chemistry,
University of Umeå, S-901 87 Umeå, Sweden

ABSTRACT

PCDDs and PCDFs have been identified in samples of biota all around the world. The concentrations in air, soil and sediment samples are dependent on the locations. Ecotoxicological effects are reported for fish, fish eating birds as well as marine and freshwater mammals.

ENVIRONMENTAL CONCENTRATIONS

Biota

The 2,3,7,8-substituted tetra-, penta- and hexachlorinated PCDDs and PCDFs bioaccumulate and bioconcentrate like other stable lipophilic pollutants. The non 2,3,7,8-substituted congeners are metabolized and/or excreted much faster and are normally not found in biological samples. Exception from this rule are the classes of crustaceans and molluscs and possibly also other lower organisms in which most congeners are retained. These lower animals are good indicators for point sources. The hepta- and octa-chlorinated congeners have low assimilation efficiencies despite their high lipophilicity, which is believed to be due to their large molecular size which hinders the transfer over membranes. For all PCDDs and PCDFs the levels are normally much higher in aquatic animals than in terrestrial.

A large number of analyses have now been performed and PCDDs as well as PCDFs have been identified in biological samples collected from all around the world including the Arctic and Antarctic. The concentrations vary with species, type of tissue, age group, body mass, fat content, season and location. The concentrations found in fish caught well offshore are generally much lower than in those caught in the vicinity of the coast.

The highest levels reported so far are found in samples of crab, lobster and bass from the Newark Bay, New Jersey, USA (1). Here values exceeding 6 000 pg/g fresh weight are found in the hepatopancreas of a crab, see Table 1.

Table 1. Concentrations in samples from Newark Bay in pg/g fresh weight

	Crab hep.*	Crab meat	Lobster hep.*	Bass
2,3,7,8-TCDD	6200	110	610	730
2,3,7,8-TCDF	672	15	380	86
2,4,6,8-TCDT**	>8300	>150	1000	50

* hepatopancreas ** 2,4,6,8-tetrachlorodibenzothiophene

In the crustacean samples from this location the dominating congener was 2,4,6,8-tetrachlorodibenzothiophene, but this compound was only a minor peak in the bass fish sample (2). This compound is probably non-toxic, but could serve as a useful indicator of the pollution source in this specific highly contaminated area.

Abiotic samples

Background concentrations of PCDDs and PCDFs have been reported in a series of abiotic reservoirs like soil and sediments but also in air and snow. These matrices will be discussed below. The patterns found in these samples are the typical combustion pattern, indicating various combustion sources as the ultimate source of this worldwide contamination (3).

Air

Although inhalation is only a minor route of human exposure to PCDDs and PCDFs, air measurements have been performed in many countries like Germany, The Netherlands, Sweden, and USA. A series of investigations in Germany has given the following typical concentrations of dioxins (counted as Toxic Equivalents, TEQ using the I-TEF/89 system) in ambient air: (4)

Rural areas	< 70 fg TEQ/m^3
Urban areas	71 - 350 fg TEQ/m^3
Close to major sources	351 - 1600 fg TEQ/m^3

At DIOXIN '89 in Toronto, Hunt and Maisel reported on a study from Bridgeport, Connecticut, USA (5). The samples were collected during the wintertime and large variations in the concentrations were found during the different sampling periods. The meteorological conditions were recorded at a local weather station. The authors report strong similarities in the observed congener profiles and conclude a primary influence by sources situated to the west and southwest of the sampling area: New York City. The data reported by Hunt and Maisel (5) allows a calculation of the total concentrations of PCDDs and PCDFs, the ratio as well as the TEQ, see Table 2. The dominant congeners were reported to be octaCDD, heptaCDDs and hexaCDDs while 2,3,7,8-tetraCDD was reported to be virtually non-existent. The dibenzofurans were present at lower concentrations than the PCDDs (see Table 2) and the PCDF profile was dominated by the tetra- and pentachlorinated congeners (5).

Table 2. Concentration of PCDDs and PCDFs in air samples from USA (3)

	Σ PCDDs fg/m^3	Σ PCDFs fg/m^3	Ratio PCDDs / PCDFs	TEQ fg/m^3
Minimum	217	21	10	8
Maximum	8028	2860	3	114
Average	4276	2590	1.6	105

Bolt and de Jong have performed a survey for airborne PCDDs and PCDFs in the Netherlands (6). Two of the three sampling locations were in the vicinity of MSW incinerators, and

samples were taken down-wind as well as up-wind of these incinerators. In these samples the PCDFs are found to give a larger contribution to the TEQs than the PCDDs, expecially in the down-wind samples. The relative contribution of the hepta- and octachlorinated congeners was much lower in the down-wind samples as compared to the up-wind samples (6). The concentrations were found to vary between 5 fg TEQ/m^3 and 140 fg TEQ/m^3 and the highest concentrations were found when the wind came in the direction from the incinerators. In air masses coming from the North Sea at a distance of about 30 km, the concentrations were 5 fg TEQ/m^3 and the local background level from low density urbanized areas were found to be 10-15 fg TEQ/m^3. The authors conclude that the MSW incinerator emission contributes to about 125 fg TEQ/m^3 at the local air concentrations (6).

Tysklind et al (7) report on the analysis of 14 air samples collected on the westcoast of Sweden. The total concentrations of PCDDs and PCDFs were found to vary from 344 fg/m^3 to 4110 fg/m^3, see Table 3. In most of the samples, the PCDDs were found at higher concentrations than the PCDFs. The highest concentrations were found during sampling events with air masses coming with west or southerly winds indicating long range transport of PCDDs and PCDFs. Further evidence for this was shown by the correlation between high levels of PCDDs and PCDFs and SO_2, NO_2, NO_3^-, NH_3 and soot. An interesting correlation was found in this study between the wind trajectories and the congener profiles. When the wind was coming from the north (Iceland), the congener profiles were dominated by the higher chlorinated compounds, especially octaCDD (7).

Table 3. Concentrations of PCDDs and PCDFs in air samples from Sweden (7)

Origin of the air	Σ PCDDs fg/m^3	Σ PCDFs fg/m^3	Ratio PCDDs / PCDFs	TEQ fg/m^3
UK	2380	1730	1.3	55
Germany Poland	220	150	1.4	5.6
UK, Belgium	310	200	1.5	6.1
Iceland	260	84	3.1	3.3

Soil

Soil samples have been frequently analyzed primarily in Germany and UK. Based on these studies, Printz has given the following typical concentrations (in TEQ) for soil samples in Germany (4) counted on a dry weight basis:

Rural areas	*< 10 pg TEQ/g*
Urban areas	10 - 30 pg TEQ/g
Industrial areas	30 - 300 pg TEQ/g
Close to major sources	100 - 80 000 pg TEQ/g

In 1988 Cox reported on the analysis of 77 soil samples from UK (8). After removal of 12 samples as contaminated outliers, the remaining 65 samples should represent typical background concentrations. The congener profiles in these samples are also dominated by the hepta and octaCDD. However, differences in the concentrations of more than hundred times were observed in these "background samples", see Table 4, but this problem is not further discussed.

Table 4. Concentrations in UK soil samples from ref. 8 (pg/g dry weight)

	Range	Mean
Σ Tetra CDDs	< 0.5 - 69	9.4
Σ Tetra CDFs	< 0.5 - 237	25
Σ Penta CDDs	< 0.5 - 165	6.6
Σ Hexa CDDs	2.8 - 165	38
Octa CDD	28 - 832	163

A recent study by Rotard et al (9) could explain the large variation in the UK background samples. They analyzed soil samples from plowland, grassland and forests, all representing rural background areas in Germany. They found a very interesting difference in the concentrations of PCDDs and PCDFs in these samples, the forest soil samples having much higher concentrations, see Table 5. A direct consequence is that it is of major importance to control the nature of a sampling site.

Table 5. Levels in soil samples from Germany, ref. 9 (pg/g dry weight)

	Plowland soil	Grassland soil	Forest soil
Σ Hexa CDDs/Fs	6.5 / 9.3	30.0 / 31.4	168 / 221
Σ Hepta CDDs/Fs	12.3 / 11.3	74.7 / 34.5	247 / 224
Octa CDD/F	30.0 / 15.3	211 / 35	348 / 276

The authors explain this interesting observation to be due to the filtering effect through adsorption of PCDDs and PCDFs by conifer needles and leaves. It has recently been found that the PCDD and PCDF concentrations increase during composting of garden wastes(10). Since composting is quite normal in forests, this might also contribute to the increased levels in forest soil samples.

Sediment

Analysis of sediments can give valuable information concerning the spatial variation of contamination, and sediment cores can be very useful to investigate historical trends. As PCDDs

and PCDFs are fat soluble or bound to organic particulate matter, the best way to obtain comparability between different sediments is to relate the concentrations to the organic matter by means of loss of ignition (LOI). However, up to now most data are reported on a dry weight basis. The concentrations vary greatly due to local point sources, see Table 6, where some reported data based on LOI are collected and compared. In the Dala River the concentrations of octaCDD increase by a factor of close to hundred from Grövelsjön to Hedesundafjärden, but now obvious source has been identified in this river system.

Table 6. Concentrations of hepta- and octachlorinated congeners and TEQ in sediments (pg/g LOI).

	Elbe River,Germany (11)		Dala River, Sweden (12)				Lake Vättern,Sweden (12)	
	SB**	BH***	GS**#	Siljan	Hovran	HF#	Hjo	Motala
HpCDF*	8214	11130	98	1030	110	630	690	130
HpCDD*	4800	12500	59	160	200	2180	870	230
OCDF	35140	56600	260	4250	150	190	700	170
OCDD	22860	69000	180	810	2960	16830	1890	800
TEQ	772	1000	13	37	19	180	190	38

* The 1,2,3,4,6,7,8-substituted congeners
** Schmeckenburg *** Bunthaus harbor
**# Grövelsjön # Hedesundafjärden

Sediments collected in the Baltic Sea outside a Swedish pulp mill showed a very good correlation of several PCDD and PCDF congeners and the distance from the pulp mill (13). A very good correlation was also found for the mono- and dimethyl substituted PCDFs (R-PCDFs) which are present at levels 10-1000 times higher than the normal PCDFs and PCDDs (14). These compounds have been used in our laboratory as good indicators in sediment samples of pulp bleaching using free chlorine gas.

Bopp et al (15) analyzed sediments and suspended matter in Newark Bay, New Jersey, USA. Present and historical levels of 2,3,7,8-tetra CDD were established and concentrations up to 21 000 pg/g were found in sediments deposited near an industrial site in Newark, where chlorinated phenols had been produced. The conclusion is drawn that this chemical manufacturing is the dominant source in the area (15). Using principal component analyses of the data, this conclusion has been questioned (16). However, it is amazing to find that the existence of the indicator 2,4,6,8-tetrachlorodibenzothiophene found in crustaceans from this area (1, 2) is completely neglected in this discussion.

ECOTOXICOLOGICAL EFFECTS

Adverse effects in several wildlife species have been correlated with environmental exposure to PCDDs, PCDFs and PCBs. The effects observed in field studies are consistent with those

found in laboratory animals, however the possible contribution of other chemicals to these effects is difficult to rule out. The case histories discussed are related to the contamination of aquatic food webs and almost all come from enclosed locations with low rates of water exchange like the Baltic Sea, the Wadden Sea, the Great Lakes, and the Puget Sound at the US/Canadian Pacific coast.

Fish

Dioxins and related compounds may have an adverse effect on the reproduction of fish. Laboratory experiments have shown that several fish species including lake trout are extremely sensitive to 2,3,7,8-tetra CDD and similar compounds (17). The toxic response of some of the most toxic PCDDs, PCDFs and PCB showed to be additive (18). In most of the fish species that have been studied, the hallmark sign is sac fry endema and mortality (17,18). Similar symptoms have been reported for many wild populations of fish including lake trout in the Great Lakes and for the atlantic salmon in the Baltic Sea, the M-74 syndrome. In 1993, the mortality in the sac fry stage in most Swedish hatcheries have exceeded 80%. However, it is still unclear if PCDDs, PCDFs, PCBs and related compounds have a role in this mortality. After more than 15 years of reluctance from the responsible Swedish authorities, the decision has now been made to support scientific studies of the M-74 syndrome.

Fish-eating birds

The effects of PCDDs, PCDFs and PCBs on birds have been extensively studied. Field studies have been undertaken on a variety of wild bird species to investigate whether PCDDs, PCDFs and PCBs have caused reproductive dysfunction or other lesions. An excellent review of these incidents, primarily in the Great Lakes, has been published by Gilbertson (19).

More recently, a colony of Foster's tern on Green Bay, Wisconsin, USA has exhibited symptoms of embryotoxicity, congenital deformities and poor hatching success. The available data now support the conclusion that dioxin-like effects of various planar halogenated hydrocarbons are responsible for the intrinsic reproductive problems noted in this colony (20,21).

Marine and freshwater mammals

The possible role of PCBs, PCDDs, PCDFs and related compounds in the decline of some populations of marine and freshwater mammals has been studied intensively since the early 1970s, see Gilbertson (19).

The three species of seals; grey seal, harbor seal and ringed seal, have all suffered from a dramatic decline in population number in the Baltic Sea and the North Sea during the present century. Pathological changes in the female reproductive tract, in adrenals, bone tissue and the alimentary tract have been found in seals from the Baltic Sea. There is a general agreement that the health problems in the Baltic Sea are related to the presence of PCBs and other related halogenated pollutants (22). These observations led to a four year research project financed jointly by the Swedish EPA and WWF.

Two commercial PCB mixtures have been tested *per se* and also after fractionation into four fractions consisting of

a) di-, tri- and tetraortho chlorine substituted PCBs
b) mono-ortho chlorine substituted PCBs
c) non-ortho chlorine substituted PCBs
d) a fraction of di- and tricyclic contaminants like PCN and PCDFs.

These fractions were used in a feeding study to investigate the reproduction of mink (23). The exposure to the PCB mixture as well as to one or more of the PCB fractions did not significantly influence the implantation rate. However, the exposure to the PCB mixture as well as to a combination of two or more PCB fractions generally increased the rate of interrupted pregnancies and decreased the number of living whelps born as well as the litter size. Exposure to the PCDF/PCN fraction unexpectedly resulted in significantly higher number of living whelps as well as an increase in the survival rate (23).

The concentrations of PCDDs and PCDFs were found to be low for both grey seal and harbor seal from the Baltic Sea indicating a fast metabolism or a less efficient uptake. These concentrations were lower than those found for herring and salmon from the same area. Moreover, the non- and mono-ortho substituted PCBs behaved in a similar way while the concentrations of the other PCBs, which are believed to be non-toxic, as well as DDTs appear to be one to two order of magnitude greater in seal blubber than in the extractable lipids of fish from the same area (24). However, the absence of PCDDs and PCDFs and toxic PCBs in the seal blubber does not exclude the possibility that this group of compounds also contribute to the toxic response found in these animals. The concentrations of PCBs indicate a high exposure to all contaminants present in the feed.

The relative amount of the metabolites, PCB-methyl sulfones, was comparatively high in diseased Baltic seals. Methyl-sulfonyl metabolites of both PCB and DDE have been found in considerable amounts in seal adrenals, and DDE-methyl sulfones have been shown to have strong toxic effects on mammalian adrenal tissue (24). This indicates that it is important to further investigate this group of metabolites.

REFERENCES

1. Rappe C, Bergqvist P-A, Kjeller L-O, Swanson S, Belton T, Ruppel B, Lockwood K and Kahn PC. Chemosphere, 1991, 22, 239-266.
2. Buser H-R and Rappe C. Anal.Chem., 1991, 63, 1210-1217.
3. Rappe C. Chemosphere, 1993, 27, 211-225.
4. Prinz B. Current Views on the Impact of Dioxins and Furans on Human Health and the Environment. The Toxicology Forum, Berlin, Germany 1992, 418-435.
5. Hunt GT and Maisel BE. Chemosphere, 1990, 20, 1455-1462.
6. Bolt A and de Jong APJM. Chemosphere, 1993, 27, 73-81.
7. Tysklind M, Fängmark I, Marklund S, Lindskog A, Thaning L and Rappe C. Env.Sci.Technol. In press.
8. Cox BA. Waste Management Bulletin, 1988, 16, 9-11.
9. Rotard W, Christmann, W and Knoth W. Budesgesundheitsamt, D-1000 Berlin 33, Germany, unpublished results.
10. Öberg L, Wågman N, Andersson R and Rappe C. Abstract DIOXIN '93, Vienna.

11. Götz R, Friesel P, Rock K, Päpke O, Ball M and Lis A. Chemosphere 1993, 27, 105-111.
12. Kjeller L-O, Kulp S-E, Bergek S, Boström M, Bergqvist P-A, Rappe C, Jonsson B, de Wit C, Jansson B and Olsson M. Chemosphere 1990, 20, 1489-1496.
13. Jonsson P, Rappe C, Kjeller L-O, Kierkegaard A, Håkansson L and Jonsson B. Ambio1993, 22, 37-43.
14. Buser H-R, Kjeller L-O, Swanson S and Rappe C. Env.Sci.Technol. 1989, 23, 1130-1137.
15. Bopp RF, Gross ML, Tong H, Simpson J, Monson SJ, Deek BL and Moser FC. Env.Sci.Technol. 1991, 25, 951-956.
16. Wenning R, Paustenbach D, Johnson G, Ehrlich R, Harris M and Bedbury H. Chemosphere 1993, 27, 55-64.
17. Peterson RE, Current Views on the Impact of Dioxins and Furans on Human Health and the Environment. The Toxicology Forum, Berlin, Germany 1992, 383-399.
18. Bol J, van den Berg M and Seinen W. Chemosphere 1989, 19, 899-906.
19. Gilbertson M in Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products, Kimbrough R and Jensen AA, Eds. Elsevier Amsterdam-New York 1989, 103-127.
20. Kubiak TJ, Harris HJ, Smith LM, Schwartz TR, Stalling DL, Trick JA, Sileo L, Docherty DE and Erdman TC. Arch.Environ.Contamin.Toxicol. 1989, 19, 706-727.
21. Tillitt DE, Kubiak TJ, Ankley GT and Giesy JP. Chemosphere 1993, 26, 2079-2084.
22. Jonels A. Ambio 1992, 21, 493.
23. Kihlström JE, Olsson M, Jensen S, Johansson Å, Ahlbom J and Bergman Å. Ambio 1992, 21, 563-569.
24. Olsson M, Andersson Ö, Bergman Å, Blomkvist G, Frank A and Rappe C. Ambio 1992, 21, 561-562.