

# Sources and environmental concentrations of dioxins and related compounds

Christoffer Rappe

*Institute of Environmental Chemistry, Umeå University, S-901 87 Umeå, Sweden*

**Abstract:** Polychlorinated dioxins and dibenzofurans are two series of tricyclic aromatic compounds, which have been in the focus of the interest the last decades; in all there exist more than 200 congeners. They are formed in numerous sources, primarily in incineration processes and in industrial processes. It has also been found that they are formed by natural processes. They are ubiquitous all over the world, and they have been quantified in abiotic samples like soil, sediments and air as well as in living organisms, primarily aquatic organisms. A dramatic decrease in most environmental concentrations including biological and human samples of PCDDs and PCDFs has been identified. There is a discrepancy between sources and environmental reservoirs which cannot be fully explained.

## INTRODUCTION

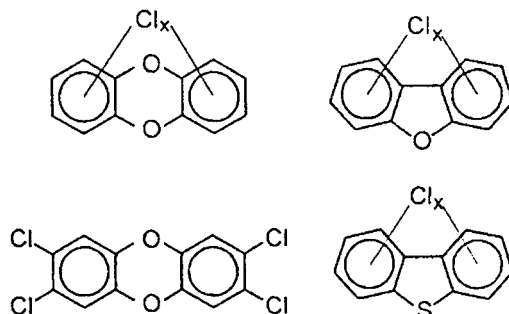
Polychlorinated dibenzo-*para*-dioxins (PCDDs) and dibenzofurans (PCDFs) are chlorinated aromatic compounds with similar chemical properties. All are solids with high melting and boiling points, limited solubility in water and low vapour pressure. The structures of the parent compounds are given in Fig. 1.

A large number of different combinations of both the number of chlorine atoms and position of substitution is possible, and as a result there are 75 different PCDD and 135 PCDF, or altogether 210 different compounds. There are more PCDFs than PCDDs because the single oxygen atom makes the furan molecule less symmetrical than the corresponding dioxin and hence there are more possible patterns of substitution. The number of isomers of PCDDs and PCDFs for a certain number of chlorine atoms is given in Table 1.

The toxicity varies substantially among the different PCDDs and PCDFs. It is generally accepted that *only 17 out of the 210 dioxin and dibenzofuran congeners are toxic*. The congener with the greatest toxic potency, and for which the greatest amount of toxicological information is available is 2,3,7,8-tetra-CDD, see Fig. 1. Environmental media as well as biological samples contain varying mixtures of PCDD and PCDF congeners of varying toxicity. Many congeners are present at substantially greater concentrations than 2,3,7,8-tetra CDD, and exposure or risk assessment of these PCDDs and PCDFs should consider all the congeners present. To facilitate comparisons of different sources or environmental media in which the congener mixtures vary, it is important that such mixtures of dioxins and dibenzofurans be assessed in a

**Table 1** Number of PCDD and PCDF isomers

| Number of chlorine atoms | Number of PCDD isomers | Number of PCDF isomers |
|--------------------------|------------------------|------------------------|
| 1                        | 2                      | 4                      |
| 2                        | 10                     | 16                     |
| 3                        | 14                     | 28                     |
| 4                        | 22                     | 38                     |
| 5                        | 14                     | 28                     |
| 6                        | 10                     | 16                     |
| 7                        | 2                      | 4                      |
| 8                        | 1                      | 1                      |
| Total                    | 75                     | 135                    |



**Fig. 1** Structural formulas of PCDDs, PCDFs, 2,3,7,8-tetraCDD and PCDTs.

**Table 2** Proposed I-TEF-factors for PCDD and PCDF [Ref. 1]

| Isomer                 | I-TEF | Isomer                 | I-TEF |
|------------------------|-------|------------------------|-------|
| 2,3,7,8-TCDD           | 1.0   | 2,3,7,8-tetraCDF       | 0.1   |
| 1,2,3,7,8-pentaCDD     | 0.5   | 1,2,3,7,8-pentaCDF     | 0.05  |
| 1,2,3,4,7,8-hexaCDD    | 0.1   | 2,3,4,7,8-pentaCDF     | 0.5   |
| 1,2,3,6,7,8-hexaCDD    | 0.1   | 1,2,3,4,7,8-hexaCDF    | 0.1   |
| 1,2,3,7,8,9-hexaCDD    | 0.1   | 1,2,3,6,7,8-hexaCDF    | 0.1   |
| 1,2,3,4,6,7,8-heptaCDD | 0.01  | 1,2,3,7,8,9-hexaCDF    | 0.1   |
| OctaCDD                | 0.001 | 2,3,4,6,7,8-hexaCDF    | 0.1   |
|                        |       | 1,2,3,4,6,7,8-heptaCDF | 0.01  |
|                        |       | 1,2,3,4,7,8,9-heptaCDF | 0.01  |
|                        |       | OctaCDF                | 0.001 |

scientifically sound and standardized manner. In an attempt to achieve these objectives, the TEF/TEQ approach has been adopted internationally. Numerical Toxic Equivalent Factors (TEFs) have been developed, which enables the conversion from the concentrations of mixtures of various congeners to toxic equivalent (TEQ) concentrations of 2,3,7,8-tetraCDD based

on their concentration to the toxicity [1]. In Table 2 the current International Toxic Equivalent Factors (I-TEFs) for the 17 toxic dioxins and dibenzofurans are given.

The TEF approach can be used to transform analytical results of total sum of all PCDDs and PCDFs into toxic equivalents (TEQ)s. The amount of each congener in a sample is converted using the TEFs to the amount of 2,3,7,8-tetraCDD that would have produced the same effect using the TEFs. For example a PCDD, present at the concentration [S] that is half as toxic as 2,3,7,8-tetraCDD is converted to TEQ as follows:  $TEQ = 0.5 [S]$ . The TEQ for a sample containing 20 pg 2,3,4,7,8-penta CDF/g (TEF = 0.5) is:  $0.5 \times [20]$  equals 10 pg TEQ/g.

## SOURCES

It is now well established that PCDDs and PCDFs are ubiquitous all over the world, even in the Arctic and Antarctica [2]. They undergo long-range aerial transport [3].

Environmental contamination by PCDDs and PCDFs can be attributed to a series of primary sources which are described below, while human exposure is due to secondary sources including food intake, (> 95%), drinking water, inhalation of air and dermal contact. Other secondary sources are abiotic reservoirs like soil and sediments.

The identified primary sources are mainly anthropogenic, but natural formation of PCDDs and PCDFs has also been described, see below. The primary sources can be divided into four categories.

During many *chemical reactions* it has been found that PCDDs and PCDFs are formed as unwanted byproducts. As a result many pesticides and industrial-chemical products, including chlorophenols and chlorophenoxy herbicides (2,4,5-T) and PCBs have been strictly regulated or banned in recent years. Another chemical process generating PCDDs and PCDFs is the bleaching of pulp with chlorine gas. The dioxin problem in the pulp bleaching was first reported in 1986 at DIOXIN '86 [4]. The major interest was concentrated on 2,3,7,8-tetraCDD and 2,3,7,8-tetraCDF, although 1,2,7,8-tetraCDF could be a useful indicator for pulp bleaching. An intense research program was started primarily in Scandinavia, USA and Canada, and the dioxin problem was correlated to the use of chlorine gas in the bleaching. The introduction of chlorine dioxide as a bleaching agent has eliminated the formation of 2,3,7,8-tetraCDD and related compounds [5–7]. All pulp mills in Sweden are now using chlorine dioxide (ECF pulp) or nonchlorinated reagents (TCF pulp) in their bleaching process.

*Combustion processes* are considered to be another important primary source of PCDDs and PCDFs. Most thermal reactions which involve burning of chlorinated organic or inorganic compounds result in the formation of PCDDs and PCDFs. Of special importance is the incineration of various types of wastes like municipal (MSW), hospital and hazardous wastes and the production of iron and steel and other metals (copper, magnesium, nickel). Some thermal sources may be natural, for example forest fires and burning

of sea-weeds containing common salt, but the background levels associated with these processes are relatively low [8,9].

The dioxin problem generated during the incineration of MSW was first identified in 1977 [10,11]. In 1986 Swedish authorities introduced an emission limit of 0.1 ng TEQ/m<sup>3</sup> for new incinerators and 0.5–2 ng TEQ/m<sup>3</sup> for existing incinerators [12]. This means a reduction of hundred to thousand times, which has been achieved by the introduction of new technology. This technology is based on improved combustion and on various types of dry, semi-dry, or wet scrubbing techniques. These incinerators meet the requirement of the 'three Ts' [13]:

- Temperature above 850 °C;
- Time (residence) typically 2 s or longer in the hot zone;
- Turbulence improved by furnace geometry and secondary air.

Most of these modern incinerators are equipped with flue gas cleaning devices based on dry scrubbing with addition of lime and charcoal followed by fabric filters [13].

A question receiving much attention concerns the influence by various chlorinated compounds such as PVC in the wastes being incinerated. In an EC report it is stated that no data are available to prove that elimination of chlorinated compounds like PVC, would highly reduce the dioxin emissions [13]. Very recent incineration experiments under controlled conditions with no carry-over effects confirm this conclusion [14].

In 1986 we reported that PCDDs and PCDFs could be identified in dust from a steel mill in Sweden at levels of 800 pg TEQ/g dust [15]. At DIOXIN '88 (in Umeå) we also reported on a study in a pilot plant where scrap metal was melted and recycled. Using a batchwise charging, the collected smoke contained 110 ng TEQ/m<sup>3</sup> [16]. The Swedish EPA considers the production of iron and steel to be the major source of PCDDs and PCDFs in Sweden in the 1990s [17].

In 1991 it was found that sintering plants in Sweden and in the Netherlands are dioxin sources [13]. One single sintering plant in the Netherlands was emitting 24 g TEQ per year [19]. It has also been found that dust from foundries can be contaminated by PCDDs and PCDFs at levels up to 22 700 pg TEQ/g dust.

It is interesting to notice that the specific congener patterns found in these samples from the iron and steel industry are very similar to those which constitute the typical incineration pattern, with the exception that the PCDFs are present at much higher levels than the PCDDs, primarily the tetra- and pentaCDFs. In addition a series of chlorinated dibenzothiophenes (PCDTs), see Fig. 1, have been identified in the sintering plants and the foundries at approximately the same levels as the PCDFs. The PCDTs have the same nominal masses as the PCDDs, but these two groups of pollutants can be effectively distinguished by MS/MS technique [20].

*Photochemical reactions* under atmospheric conditions or aerial transport can result in the formation of PCDDs and PCDFs, as well as in the degradation of these compounds. These reactions are of special interest, since most combustion and incineration sources produce emissions that undergo long-range transport [3].

Besides non biological formation processes, *some biological processes* can result in the formation of PCDDs and PCDFs. Our first example including mixing of chlorophenols, hydrogen peroxide and a series of peroxidases at room temperature resulted in the formation of PCDDs and PCDFs. Later on, in addition to this evidence from *in vitro* experiments, these reactions can also occur under true *in vivo* or environmental conditions such as in sewage sludge and compost [21,22].

## NATIONAL SOURCE INVENTORIES

Due to the interest by the public and in mass media, several countries have performed national source inventories for dioxins to eliminate the major sources and minimize the potential risk for the environment. The first source inventory for air emissions was performed in 1990 by the Swedish EPA [17]. The dominating source was MSW incineration followed by iron, steel, and non-ferrous metal works, pulp mills and exhaust gases from cars running on leaded gasoline containing halogenated scavengers. A substantial decrease in these emissions was postulated for the 1990s primarily due to the introduction of new technology for the MSW incineration but also the introduction of new technology for pulp bleaching and unleaded gasoline without halogenated scavengers. The major dioxin source for PCDDs and PCDFs in Sweden in the mid 90s should be the metal production and the metal treatment [17].

**Table 3** Values of TEQ in samples of air, aerial deposition and soil in Germany [25]

|                        | Air<br>fg/m <sup>3</sup> | Deposition<br>pg/m <sup>2</sup> , d | Soil<br>pg/g |
|------------------------|--------------------------|-------------------------------------|--------------|
| Rural areas            | < 70                     | 5–22                                | < 10         |
| Urban areas            | 71–350                   | 10–100                              | 10–30        |
| Industrial areas       | –                        | –                                   | 30–300       |
| Close to major sources | 351–1600                 | 123–1293                            | 100–80 000   |

A more detailed inventory has been performed by Bremmer *et al.* for the Netherlands [19]. In 1992 they found the major source in this country to be MSW incineration, but in the year 2000 they consider the earlier use of pentachlorophenol (banned already in the 1980s) to be the major source. The material treated with pentachlorophenol will still be in use in year 2000.

Recently HMIP [23] published an estimated inventory of emissions of PCDDs and PCDFs to the atmosphere in UK. The dominant source was the incineration of municipal solid waste (MSW) contributing an average of 70% of the emission from industrial sources. Other major emissions are

- emission from sinter plants (steel mills);
- combustion of coal;
- emission from iron and steel plants;
- emission from non-ferrous metal operations;
- combustion of clinical waste.

Collectively these five emission sources contribute an average of 23% to total industrial emissions in roughly equal proportions. The total estimated emissions into the air in UK are 560–1100 g TEQ per year.

## ENVIRONMENTAL CONCENTRATIONS

### 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. Air, soil and sediments will be discussed below. The patterns found in these samples are the typical combustion patterns, indicating various combustion sources as the ultimate source of this worldwide contamination [24].

#### 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 annual PCDD and PCDF values for air and aerial deposition in ambient air, as given in Table 3 [25].

Bolt & de Jong have performed a survey for airborne PCDDs and PCDFs in the Netherlands [26]. 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

**Table 4** Concentrations of PCDDs and PCDFs in air samples from Sweden [3].

| Origin of<br>the air | $\Sigma$ PCDDs<br>fg/m <sup>3</sup> | $\Sigma$ PCDFs<br>fg/m <sup>3</sup> | Ratio          |                          |
|----------------------|-------------------------------------|-------------------------------------|----------------|--------------------------|
|                      |                                     |                                     | PCDDs<br>PCDFs | TEQ<br>fg/m <sup>3</sup> |
| 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                      |

**Table 5** Mean values of PCDDs, PCDFs, TEQ (ng/kg) and ratio (PCDDs/PCDFs) in soil from Germany [27].

|                   | Plowland | Grassland | Forest<br>Deciduous | Forest<br>Coniferous |
|-------------------|----------|-----------|---------------------|----------------------|
| Hexa CDDs         | 7.0      | 14.9      | 202                 | 156                  |
| Hexa CDFs         | 10.7     | 15.2      | 229                 | 170                  |
| Hepta CDDs        | 14.2     | 25.7      | 275                 | 220                  |
| Hepta CDFs        | 12.3     | 17.8      | 245                 | 187                  |
| Octa CDD          | 32.3     | 43.6      | 283                 | 320                  |
| Octa CDF          | 17.7     | 23.6      | 380                 | 167                  |
| TEQ               | 1.7      | 2.3       | 38.0                | 36.9                 |
| Ratio PCDDs/PCDFs | 0.84     | 1.0       | 0.60                | 0.65                 |

contribution to the TEQs than the PCDDs, especially 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. The concentrations were found to vary between 5 fg TEQ/m<sup>3</sup> and 140 fg TEQ/m<sup>3</sup> 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<sup>3</sup> and the local background level from low density urbanized areas were found to be 10–15 fg TEQ/m<sup>3</sup>.

Similar results were reported by Tyskling *et al.* [3] 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<sup>3</sup>–4110 fg/m<sup>3</sup>, see Table 4. 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<sub>2</sub>, NO<sub>2</sub>, NO<sub>3</sub>, NH<sub>3</sub><sup>-</sup> 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 [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 counted on a dry weight basis are given in Table 3 [25].

In a recent study by Rotard *et al.* [27] soil samples from plowland, grassland and forests, all representing rural background areas in Germany, were analyzed. They found a very interesting difference in the concentrations, the highest values were found for forest soil, see Table 4. A direct consequence is that it is of major importance to control the nature of a sampling site.

The authors explain this interesting observation to be due to the filtering effect through adsorption of PCDDs and PCDFs by conifer needles and leaves. The ratio PCDDs/PCDFs found in these German soil samples is more similar to the ratio found in air samples close to a local point source [26] and in air samples not undergoing transatlantic long range transport, see Table 4 [3]. Consequently the ultimate source for the PCDDs and PCDFs found in these German soil samples are local, national or from the European continent.

### 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, see below. 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 [28]. In the Dala River the concentrations of octaCDD increase by a factor of close to hundred from the upper part to the lower part, but no obvious source for octaCDD has been identified in this river system. The

**Table 6** Concentrations of hepta- and octachlorinated congeners and TEQ in sediments (pg/g LOI) from ref. 28.

|        | Elbe River, Germany |        | Dala River, Sweden |        |             |
|--------|---------------------|--------|--------------------|--------|-------------|
|        | SB**                | BH***  | GS***#             | Siljan | Hovran HF   |
| HpCDF* | 8214                | 11 130 | 98                 | 1030   | 110 630     |
| HpCDD* | 4800                | 12 500 | 59                 | 160    | 200 2180    |
| OCDF   | 35 140              | 56 600 | 260                | 4250   | 150 190     |
| OCDD   | 22 860              | 69 000 | 180                | 810    | 2960 16 830 |
| TEQ    | 772                 | 1000   | 13                 | 37     | 19 180      |

\* The 1,2,3,4,6,7,8-substituted congeners

\*\* Schmeckenburg; \*\*\* Bunthaus harbor

\*\*\*# Grövelsjön (upper part); # Hedesundafjärden (lower part)

lower part of the Dala River (Hedesundafjärden) is a slow floating system with thick layers of soft sediments.

A similar situation has been reported for a river system in southern USA [29]. The concentrations of octa- and hepta CDDs were found to increase dramatically in sediments collected inside a national forest, where there are no known anthropogenic impact. A more likely explanation is non-anthropogenic sources. This area is covered by wetlands and swamps. Concentrations of octa CDD exceeding 350 000 pg/g LOI were found in this area, which is approximately five times more than in sediments in the highly polluted River Elbe in Germany in Hamburg harbor.

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. 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. These compounds have been used in our laboratory as good indicators in sediment samples of pulp bleaching using free chlorine gas [30].

Bopp *et al.* 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 in the 1960s. The conclusion is drawn that this chemical manufacturing is the dominant source in the area [31].

### 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

**Table 7** Concentrations in samples from Newark Bay in pg/g fresh weight [32]

|                | 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-TCDF** | >8300      | >150      | 1000          | 50   |

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

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, where high sediment concentrations were also found. Here values exceeding 6000 pg/g fresh weight are found in the hepatopancreas of a crab, see Table 7 [32].

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. This compound is probably non-toxic, but could serve as a useful indicator of the pollution source in this specific highly contaminated area.

## HISTORICAL TRENDS

For the risk assessment and risk management of PCDDs and PCDFs it is of fundamental importance to investigate the time trends of these compounds. A number of matrices can be used for this purpose, some of these respond very slowly like soil samples, other more quickly like dated layered sediments and herbage which only receives aerial deposition.

A series of archived unwashed herbage samples from the same plot in UK have been collected between 1861 and the present. The analyses showed that the concentrations remained essentially constant between 1861 and 1945, then rose to two peaks in 1961–65 and 1976–80. Since then the concentrations have declined and the 1991–93 sample was similar to that of the pre-1946 sample, see Fig. 2. The declining concentrations are much more pronounced for the PCDDs than for the PCDFs, which is explained by the restrictions of the use of pentachlorophenol in several European countries [33].

Ten guillemot eggs have been collected at an island in the Baltic Sea each year from 1969. Analyses of pooled samples indicate a downgoing trend for all PCDDs and PCDFs. The concentrations in the mid 1990s are » 20–25% of the concentrations found 1969 [34].

P. Fürst has followed the concentrations of PCDDs and PCDFs in human milk from Germany. During the period 1989–1993 the values counted as TEQ decreased by 50% [35] (Fig. 2).

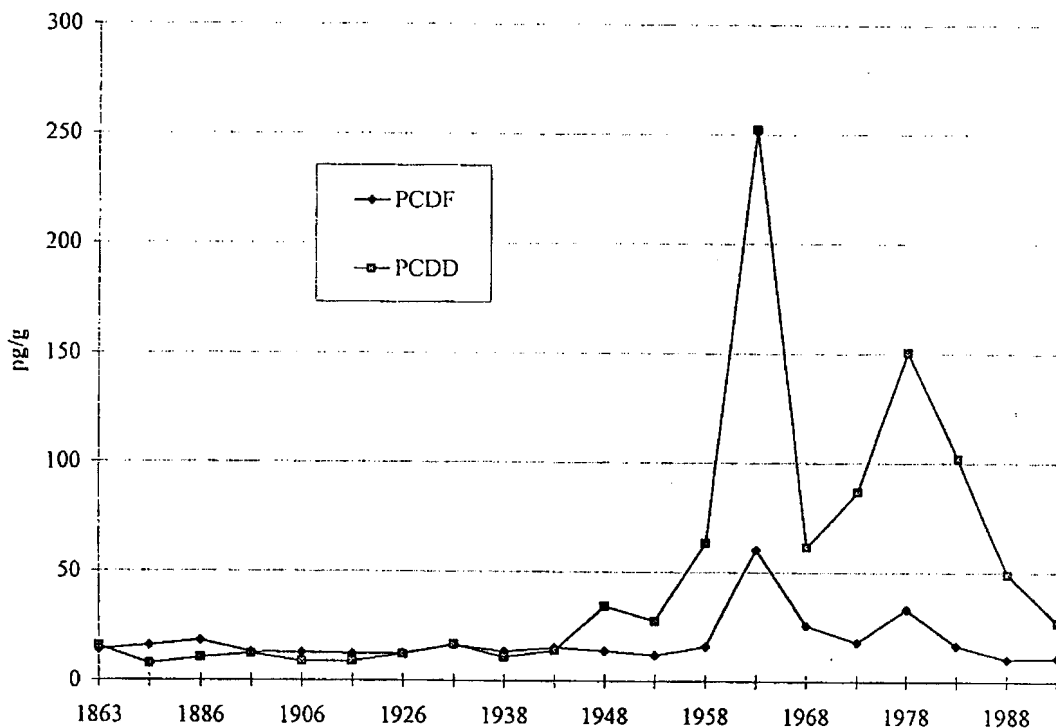


Fig. 2 Trends of PCDDs and PCDFs in herbage sample from UK [33].

## COMPARISON SOURCES—DEPOSITIONS—RESERVOIRS

Now we have a large database regarding levels, patterns and profiles of PCDDs and PCDFs in various samples representing sources, deposition matrices and reservoirs, but up to now very few detailed comparisons have been made between the different types of matrices.

As discussed above, there is a very good correlation of the pattern between samples from various combustion sources and abiotic reservoirs. If the comparison is expanded to include the congener profiles as well, the situation is much more complex. The term profile refers to the ratio of the sum of all iso-mers within a group. The comparison between chimney soot from wood burning and a sample of air particulates published [36], is excellent for such a comparison due to the fact that it includes all chlorination levels. The sources are dominated by the lower chlorinated congeners, in particular the mono- to tetraCDFs, while the particulate sample is dominated by the hepta- and octachlorinated congeners. For instance the ratio tetraCDDs/octaCDD in the soot sample is 43.3, but for the particulate 0.0048. The corresponding ratios for the chlorinated furans are 191.4 and 0.22.

It has been suggested that this dramatic difference could be explained by a greater tendency for vaporization and a preferential photodegradation of the lower chlorinated congeners [37]. If this is the case, the net result should be a very dramatic decrease in the total amounts of the toxic Cl<sub>4</sub>–Cl<sub>6</sub> substituted PCDDs and PCDFs as well as TEQ during transport processes. The amount emitted by the sources should be much larger than the amounts reaching the reservoirs. This is not the case [24].

This discrepancy between sources and reservoirs cannot be fully explained. Part of the explanation could be in unknown sources, for instance wood burning and enzymatic reactions. Moreover, it cannot be excluded that other environmental reactions do exist, which will result in a transformation into octaCDD and the higher chlorinated congeners.

## CONCLUSIONS

- 1 Various combustion processes are the major sources of PCDDs and PCDFs to the environment.
- 2 New technology has dramatically reduced the emission from combustion of MSW.
- 3 The introduction of unleaded gasolines has reduced the emissions in the car exhausts.
- 4 New bleaching technology has practically eliminated the emissions from pulp bleaching.
- 5 Natural formation of PCDDs and PCDFs has been proven.
- 6 The environmental concentrations of PCDDs and PCDFs show a sharp decline during the last two decades.

## REFERENCES

- 1 U.G. Ahlborg *et al.* *European J. Pharmacology* **228**, 179–199 (1992).
- 2 A. Bignert *et al.* *Chemosphere*, **19**, 551–556 (1989).
- 3 M. Tysklind, I.E. Fångmark, S. Marklund, A. Lindskog, L. Thaning, C. Rappe. *Environ. Sci. Technol.* **27**, 2190–2197 (1993).
- 4 C. Rappe. *Chemosphere* **16**, 1603–1618 (1987).
- 5 C. Rappe *et al.* *Pulp and Paper Canada* **90**, T-273–278 (1989).
- 6 P.M. Berry, B.I. Fleming, R.H. Voss, C.E. Luthe, P.E. Wrist. *Pulp and Paper Canada* **90**, T279–289 (1989).
- 7 C. Rappe, N. Wågman. *Organohalogen Compounds* **23**, 377–381 (1995).
- 8 R. Clement, C. Toshiro. Abstract S 34 DIOXIN '91. Research Triangle Park, North Carolina, USA.
- 9 L.-O. Kjeller, K.C. Jones, A.E. Johnston, C. Rappe. *Environ. Sci. Technol.* **25**, 1619–1627 (1991).
- 10 K. Olie, P.L. Vermeulen, O. Hutzinger. *Chemosphere* **6**, 455–459 (1977).
- 11 H.R. Buser, H.P. Bosshardt, C. Rappe. *Chemosphere* **7**, 165–172 (1978).
- 12 G. Bergvall. *Waste Management Research* **5**, 403–406 (1987).
- 13 Expertise on the measurements and control of dioxins. Vereniging LUCHT, NL 2600 JA Delft, the Netherlands (1991).
- 14 E. Wikström, G. Löfvenius, C. Rappe, S. Marklund. *Environ. Sci. Technol.* **30**, 1637–1644 (1996).
- 15 J. Ruuskanen, T. Vartiainen, T. Kojala, H. Manninen. *Chemosphere* **28**, 1989–1999 (1994).
- 16 M. Tysklind, G. Söderström, C. Rappe, L.-E. Hägerstedt, E. Burström. *Chemosphere* **19**, 705–710 (1989).
- 17 DIOXINS. A program for research and action. Swedish Environmental Protection Board, S-171 25 Solna, Sweden.



- 18 Swedish Dioxin Survey, open database. Swedish Environmental Protection Board, S-171 25 Solna, Sweden.
- 19 H.J. Bremmer, L.M. Troost, G. Kuipers, J. de Koning, A.A. Sein. *Rapport 770501003*, RIVM Bilthoven, The Netherlands (1993).
- 20 C. Rappe. *Fresenius' J. Anal. Chem.* **348**, 63–75 (1994).
- 21 L.G. Öberg, R. Andersson, C. Rappe. *Organohalogen Compounds*, **9**, 351–354 (1992).
- 22 L.G. Öberg, N. Wågman, R. Andersson, C. Rappe. *Organohalogen Compounds* **11**, 297–302 (1993).
- 23 HMIP. Her Majesty's Inspectorate of Pollution. A Review of Dioxin Emissions in the UK (1995).
- 24 C. Rappe. *Chemosphere* **27**, 211–225 (1993).
- 25 B. Prinz. in *Current Views on the Impact of Dioxins and Furans on Human Health and the Environment*. Berlin November 1992, 418–435.
- 26 A. Bold, A.P.J.M. de Jong. *Chemosphere* **27**, 73–81 (1993).
- 27 W. Rotard, W. Christmann, W. Knoth. *Chemosphere* **29**, 2193–2209 (1994).
- 28 C. Rappe *et al.* *Organohalogen Compounds* **12**, 163–170 (1993).
- 29 C. Rappe *et al.* *Chemosphere.*, in press.
- 30 P. Jonsson *et al.* *Ambio* **22**, 37–43 (1993).
- 31 R.F. Bopp *et al.* *Environ. Sci. Technol.* **25**, 951–956 (1991).
- 32 C. Rappe *et al.* *Chemosphere* **22**, 239–266 (1991).
- 33 L.O. Kjeller, K.C. Jones, A.E. Johnstone, C. Rappe. *Environ. Sci. Technol.* **30**, 1398–1403 (1996).
- 34 C.A. de Wit *et al.* *Organohalogen Compounds* **20**, 47–50.
- 35 P. Fürst. *Organohalogen Compounds* **13**, 1–8 (1993).
- 36 R. Bacher, M. Smerev, K. Ballschmiter. *Environ. Sci. Technol.* **26**, 1649–1655 (1992).
- 37 B. Eitzer, R. Hites. *Environ. Sci. Technol.* **23**, 1396–1401 (1989).