

Formation and Sources of PCDD/PCDF

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1. Introduction

Since the first overview on formation and sources of polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) by US-EPA scientists was published in 1980 (Esposito et al. 1980), several updates are available in the international literature (DoE 1989, Fiedler et al. 1990, Rappe 1991, Hutzinger and Fiedler 1991). The findings can be summarized as follows (Hutzinger and Fiedler 1993):

- PCDD/PCDF have never been produced intentionally but occur as trace contaminants in a variety of industrial and thermal processes.
- Due to their chemical, physical and biological stability PCDD/PCDF are able to remain in the environment for long times. As a consequence dioxins from so-called "primary sources" (once formed in industrial or combustion processes) can be transferred to other matrices and enter the environment. Such "secondary" sources are sewage sludge/biosludge, compost, or contaminated areas (e.g. Kieselrot in Germany).
- Recent research (Öberg et al. 1992, Wagner et al. 1990) identified enzymatic reactions to be responsible for the formation of PCDD/PCDF from chlorophenols.
- In wet-chemical processes the propensity to generate PCDD/PCDF during synthesis of chemical compounds decreases in the following order:

Chlorophenols < Chlorobenzenes < Aliphatic chlorinated
compounds < Inorganic chlorinated compounds

Factors favorable for the formation of PCDD/PCDF are high temperatures, alkaline media, presence of UV-light, and presence of radicals in the reaction mixture/chemical process (Hutzinger and Fiedler 1991, 1993).

- The findings established by the "Trace Chemistries of Fire" (Bumb et al. 1980) have been verified in a variety of thermal processes. Although much research has been done to study the formation of PCDD/PCDF in combustion processes, there is still no clear evidence which mechanism is dominating and which parameters are important. There is some evidence that both, homogeneous reactions in the gas phase and heterogeneous reactions on surfaces of particles play a role to form these thermodynamically stable compounds. The most important pathway for

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formation of PCDD/PCDF on fly-ash particles is when flue gases are transported at temperatures between 250 and 450 °C.

This paper briefly gives an overview the results of dioxin analyses in chemical products and recent evidence on identified sources, esp. obtained during the 2nd Toxicology Forum held in Berlin/Germany, in November 1992. As PCDD/PCDF formation can be minimized by technological means and strategies for reduction are under development this summary cannot be more than a picture of the present situation and knowledge

2. Primary Sources of Dioxins

2.1 Chemicals

Primary sources of environmental contamination with PCDD/PCDF in the past was due to production and use of chloroorganic chemicals, including the pulp and paper industry. An overview on dioxin concentrations in chemicals is given in Table 1. As can be seen from Table 1 the concentrations can vary by several orders of magnitude.

Table 1: PCDD/PCDF concentrations in chemical products

Substance	I-TEQ	Unit	Substance	I-TEQ	Unit
PCP	up to 2.32	mg/kg	<i>p</i> -Chloranil (Ger)	375.62	µg/kg
PCP-Na	up to 0.45	mg/kg	<i>p</i> -Chloranil (USA)	up to 3,065.50	µg/kg
Clophen A 30	11.32	µg/kg	<i>o</i> -Chloranil (Ger)	62.91	µg/kg
Clophen A 60	2,179.46	µg/kg	Hostaperm Violet RL (Ger)	1.20	µg/kg
2,4,6-Trichlorophenol	679.75	µg/kg	Carbazole Violet	211.43	µg/kg
Trichlorobenzene	23.33	ng/kg	Violet 23	18.9	µg/kg
Sludge from electrolysis	30.50	µg/kg	Blue 106	56.4	µg/kg

Changes in the industrial processes resulted in reduction of PCDD/PCDF concentrations in the products: e.g. an estimate for Germany says that until 1990 about 105 g I-TEQ have been introduced through use of the dye pigment Violet 23 (chloranil as intermediate). Application of a new process via hydroquinone will reduce the annual input to about 3 g I-TEQ (BGA/UBA 1993).

Since 1978-80 the Office for Agriculture and Forestry in Germany (BBA) looked for PCDD/PCDF in pesticides to be marketed (BBA 1991). The analyses were performed according to the German Ordinance on Dangerous Substances (GefStoffV, where presently limit values were set for 8 individual PCDD/PCDF congeners). Pesticides containing Dicamba, Bifenox, Lindane, Bromophos, Prochloraz gave negative results. In years 1978 to 1985 2,3,7,8-Cl₄DD could be detected in commercial mixtures on the basis of 2,4,5-T or Dichlorprop at levels up to 5 µg/kg active compound. Two pesticide

preparations from 1986 did contain 2,3,7,8-substituted PCDD/PCDF (levels <0.001 mg/kg) but no 2,3,7,8-Cl₄DD. Since 1988 none of the preparations investigated gave positive results according to German regulation; in 1987 one sample contained 0.0008 mg 1,2,3,6,7,8-Cl₆DF/kg. In all 5 preparations based on Dichlorprop, 2,4-D, or 2,4-DB from the new German federal states PCDF (up to 88 µg PCDF/kg) could be found, one sample contained detectable amounts of PCDD. Thus, application of such mixtures on agricultural land may have resulted in local contaminations.

Rappe and coworkers (Rappe et al. 1990) detected dioxins in tall acids and resins generated in the pulp industry (Tall acid: 9.5 ng I-TEQ/kg, tall resin: 200 ng I-TEQ/kg) and in liquid soap (447 pg I-TEQ/L). Detergents are suspected of being responsible for the occurrence of PCDD/PCDF in municipal sewage sludge.

2.2. Pulp and Paper

In Germany there exist exclusively sulfite mills which presently do not use molecular chlorine. Dioxin levels detected in German pulp were below 0.1 ng TEQ/kg d.m. (BGA/UBA 1993). The analysis of imported sulfate (Kraft) pulps gave concentrations in the range between 0.2 and 1.3 ng TEQ/kg d.m. Presently the import of Kraft pulp to Germany stands at 3 million tons, so that the total import of dioxins via Kraft pulp is between 0.6 and 3.9 g I-TEQ. Dioxin levels in paper products from fresh fibres generally has less than 1 ng TEQ/kg d.m. In recycling paper, however, average dioxin concentrations are between 5 to 10 ng TEQ/kg. The sources responsible for the contamination have not yet been identified completely. Print colours and additives may be possible sources (Santl 1993).

2.3 Thermal Processes

Investigations at municipal waste incinerators showed that raw gases (taken after the boiler) generally contain very low levels of PCDD/PCDF. Generation of dioxins and furans occurs as a consequence of incomplete combustion of the raw gases and fly ashes in the cooler zones (250-450 °C). Electrostatic precipitators were found to produce PCDD/PCDF. This effect was not seen for fabric filters (Vogg 1993).

Whereas in the past, the chemical industry and to a lesser extent the pulp and paper industry were considered to be the main source of dioxins and also the cause of today's contaminated sites in Germany it must be assumed on the basis of the present knowledge that thermal processes are responsible for actual dioxin input. There is still a considerable focus on waste incineration but based on the requirements set in the 17th Ordinance of the Federal Ambient Air Control Act, the annual input from MWI via exhaust gases of about 400 g TEQ per year in 1988/89 will be reduced to about 4 g TEQ at the mid 1990s. When all MWIs will meet the 0.1 ng TEQ/m³ the dioxin release will be

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reduced by 99 %. Thus, presently more attention is given to other not so intensively investigated thermal processes.

From the knowledge gained from MWIs it can be concluded that PCDD/PCDF can be formed in other thermal processes in which chlorine-containing substances are burned together with carbon and a suitable catalyst (preferably copper) at temperature above 300 °C in the presence of excess air or oxygen. Preferentially dioxin formation takes place in the zone when combustion gases cool down from about 450 °C to 250 °C (*de novo* synthesis). Possible sources of the chlorine input are PVC residues as well as chloroparaffins in waste oils and inorganic chlorine. The typical combustion pattern is characterized by the domination of the higher chlorinated dibenzo-*p*-dioxins and the lower chlorinated dibenzofuran homologues. The dioxin pattern can be changed when under conditions of insufficient oxygen (e.g. flue gas treatment) esp. the Cl₇DD and Cl₉DD undergo dechlorination to lower chlorinated homologues.

The processes investigated in more detail are (Lange 1993, BGA/UBA 1993):

- *Cable Smouldering*

Emissions of approximately 100 ng TEQ/m³ have been reported. As high levels of PCDD/PCDF have been detected in the vicinity of cable smouldering plants all thermal cable processing was finished in 1990 (today exclusively cold cable stripping).

- *Copper Recovery*

Depending on the type of furnace and the input materials, operating conditions and gas cleaning systems used, PCDD/PCDF concentrations in the off-gases may vary considerable. Most of the results obtained from industrial scale facilities in Germany were in the range of 1 to 2 ng TEQ/m³. Fabric filters are normally used for flue gas cleaning, a few plants are equipped with an afterburner.

- *Aluminum Remelting Plants*

Most processes for generation of secondary aluminum use a rotary kiln. Concentrations measured showed a wide range of emission values (0.15-13.4 ng TEQ/m³ for Al remelting plants; 0.02-21.5 as an average from 30 Al smelters). Very low levels were found in the flue gases of foundries (0.1 ng TEQ/m³). The arithmetic mean stands at about 4.4 ng TEQ/m³ and the total emissions from aluminum melting plants in Germany are estimated to be approximately 25 g TEQ per year.

Single measurements from reprocessing of lead from accumulators (contamination almost unavoidable) gave dioxin concentrations from 0.02 to more than 1 ng TEQ/m³.

- *Metallurgical Treatment of Iron Ore, esp. Sinter Plants*

The introduction of chlorine in sinter plants occurs via coke, the ore itself and other metal-containing materials involved in the process (e.g. filter dust, tinder contaminated with oil residues). Measurements from the Netherlands (PARCOM 1991) gave

PCDD/PCDF emissions of about 1-3 ng TEQ/m³. In a Swedish sinter plant they found 0.75 ng TEQ/m³ (Lexén et al. 1992).

- Melting of Iron and Steel

The melting of scrap iron and steel is mostly performed in electric arc furnaces or oxygen converters. Cupolas, induction furnaces, rotary kilns, or electric arc furnaces are used in foundries to produce iron material for casting. Relatively strict requirements are set to the amount of impurities of the scrap (free of foreign matter, including organic impurities; especially for foundries). PCDD/PCDF concentrations in the exhaust gases from iron and steel production (all charged with scrap metals) gave 0.7-9.2 ng TEQ/m³ for electric furnaces and < 0.1 ng TEQ/m³ for oxygen converters and cupolas.

- Non-metallic Industry, Manufacture of Glass and Ceramics

The input of chlorine into the processes occurs via raw materials and fuels. In these processes temperatures are usually very high and residence time long; thus the reaction conditions do not favor formation of dioxins. PCDD/PCDF emissions from rotary kilns were found to be below 0.1 ng TEQ/m³ in most cases (also when waste oil and tires were used as secondary fuels). Same results were reported from cement kilns (with waste oil) and brick kilns (with dust from saw mills, paper sludge, polystyrene as porosifier).

- Power Stations

According to several investigations emissions from power plants have been found to be much below 0.1 ng TEQ/m³; in most cases they were below 0.01 ng TEQ/m³.

- Wood Burning

Special interest is given to the burning of wood as not only natural wood but also coated wood and wood treated with organochlorines is burnt. Individual measurements gave PCDD/PCDF emissions from 0.005 to 4 ng TEQ/m³. From the results obtained it has been concluded that modern plants when burning natural wood and providing a good burn-out and efficient dust cleaning system are capable to meet the 0.1 ng TEQ/m³. Problems may occur when wood is burnt together with waste paper or cardboard.

- Crematories

Dioxin emissions up to 8 ng TEQ/m³ have been measured in the off-gases from crematories. Most crematories do not have flue gas cleaning or only cyclones for dust removal and chlorine can be introduced via the input materials; furthermore these facilities have a poor burnout.

- Landfill Gases

Despite of the high chlorine content in landfill gases burning of these gases in muffle furnaces or internal combustion engines results in relatively low dioxin emissions in the range of 0.1 ng TEQ/m³ or lower (HLfU 1991).

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- Domestic Heating

Based on the results from the LIS (1992), it is estimated that between 3.6 and 13 g TEQ are released from domestic furnaces in the 11 Old Federal States of Germany. Dioxin concentrations will be much higher if - illegally - packaging materials and other wastes are burnt in these ovens.

- Motor Vehicles

In a comprehensive study emissions of polyhalogenated dibenzodioxins and dibenzofurans have been investigated in detail. The highest concentrations were found in exhaust gases from motor vehicles using scavenger-containing leaded gasoline. Total emissions (for the 11 States of Germany) were calculated to be approximately 11 g TEQ in the year 1990. Since summer 1992 the use of scavengers in Otto fuels is prohibited in Germany. This ordinance will result in a further reduction of PCDD/PCDF emissions from motor vehicles.

3. Secondary Sources of PCDD/PCDF

Dioxin reservoirs are present as sewage sludge, compost, and liquid manure which can be used for fertilization in agriculture and gardens. Foliage represents one of the largest reservoirs as waxy leaves and needles serve as passive samplers for lipophilic compounds and additionally to dry and wet deposition "extract" dioxins and related compounds from the gaseous phase. Some data are given in Table 2.

Table 2: Overview on PCDD/PCDF Contents in Dioxin Reservoirs

Matrix	Concentration
Sewage Sludge:	
1986/87: 202	ng TEQ/kg d.m. (Range: 28-1,560 ng DM)
1990: 50-60	ng TEQ/kg d.m. (80% < 100 ng TEQ/kg = Sewage Sludge Ordinance)
Compost:	
Municipal Waste Compost:	38 ± 22 ng TEQ/kg d.m.
Blo Compost:	14 ± 9 ng TEQ/kg d.m.
Green Compost:	11 ± 8 ng TEQ/kg d.m.

4. Mass Balances

Estimates on the annual dioxin emissions from primary sources were given for several countries (see Table 3). Based on an average deposition of 12 pg I-TEQ/m²·day for rural areas there will result an annual input of about 1 kg I-TEQ to German surfaces. Taking into consideration that higher deposition rates will be found in more industrialized and populated areas about twice the amount has to be considered. This gap between calculated inputs from known sources and deposition data also occurred for other countries (Sweden, USA). So far, no explanation was found.

Table 3: Estimated annual dioxin emissions

Country	Annual Emission (g TEQ/yr.)
United Kingdom	160-930
The Netherlands	960
Sweden	120-290
Germany	~1,000
Austria (data 1990)	20-150
USA	1,214-9,923

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