Sources of PCDD/PCDF and Impact on the Environment

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1 INTRODUCTION

In contrast to other environmental pollutants, such as polychlorinated biphenyls (PCB) or DDT, polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) have never been produced intentionally for any industrial use but they occur as unwanted trace contaminants in many industrial and thermal processes. In addition to these primary sources dioxins can be released from so-called secondary sources (= reservoirs) such as landfills and contaminated areas or reenter the environment via the application of sewage sludge, compost or liquid manure. Almost all 210 individual congeners have been identified in emissions from thermal and industrial processes and consequently PCDD/PCDF are found as mixtures of individual congeners in environmental matrices such as soil, sediment, air, and plants and lower animals. PCDD/PCDF, particularly the higher chlorinated are poorly soluble in water, have a low volatility, and adsorb strongly to particles and surfaces (high K_{OC}) (for overview, see Fiedler et al. 1990). Thus, PCDD/PCDF can hardly be identified in water and are immobile in soils (des Rosiers 1986). Especially, the 2,3,7,8-chlorine substituted PCDD/PCDF are extremely stable in the environment and bioaccumulate in fatty tissues (high K_{OW}) of animals and humans.

2 Well-Known Dioxin Sources

Several surveys dealing with sources of dioxins and furans have been published within the last years (Esposito et al. 1980, Hutzinger and Fiedler 1988a, 1988b, Fiedler et al. 1990, Rappe 1993, Fiedler 1993, Hutzinger and Fiedler 1993). From the information available three main categories of dioxin sources can be identified: Chemical-industrial sources, thermal or combustion sources, and reservoirs. The industrial sources include manufacture of chlorinated chemicals, pulp and paper industry, dry cleaning distillation residues, and others. Amongst the thermal sources stationary large plants such as incinerators for municipal solid waste and hazardous waste, sewage sludge, sintering plants and various types of recycling plants have to be mentioned as well as diffuse sources such as automobile exhaust, home heating, and combustion of landfill gas. Many accidents, e.g. PCB fires, fires in buildings, forest fires, volcanoe eruptions, lead to the formation of PCDD/PCDF. Reservoirs include sewage sludge, compost, and contaminated soils. Once aware of the presence or formation of PCDD/PCDF in an industrial or thermal process measures have been undertaken to close these sources (e.g. production stop of polychlorinated biphenyls (PCB) and pentachlorophenol (PCP) in many countries) or to minimize dioxin formation by changing the production process (e.g. replacement of free chlorine gas by chlorine dioxide or chlorine-free bleaching agents in the pulp industry, primary, secondary and tertiary measures in combustion technology. Note: in the German State of Bavaria an oven of a municipal waste incinerator has to be shut down immediately when the dioxin emissions are higher than 50 ng I-TEQ/m^3).

3 New Results on Dioxin Emissions

3.1 Thermal Sources

Emissions of hazardous waste incinerators (HWI) are not as well investigated as for municipal waste incinerators (MWI). In Europe most HWI have rotary kilns assuring a good burn-out of the industrial waste. Consequently, relatively low emissions have been reported. In Bavaria PCDD/PCDF emissions of the two publicly owned HWI are between 0.8 and 6.9 ng I-TEQ/m^3. An overview on industrial waste incinerators has been compiled by the ECETOC (1992) (see Table 1).

Table 1: PCDD/PCDF emissions from industrial waste incinerators (ng TEQ/m^3) (ECETOC 1992). * PCDM = Polychlorodiphenylmethane

Location	Start of Operation	Emission	Remarks
Schwabach, Germany	1965 (?)	0.8-0.9	
Ciba-Geigy, Basel, Switzerland	1972	0.018	Pilot plant, multistage scrubber
Nybørg, Denmark	1974	5.8	1987
Ebenhausen, Germany	1975	5.8	1989
		5.6-6.9	1990
Biebesheim, Germany	1976	0.37	without PCB
		0.45	100 kg PCB added
		0.5-1	without PCB
Bayer AG, Brunsbüttel, Germany	1982	0.66	Trial burn; 8.4 kg/h PCB + 63.0 kg PCDM*added
		0.059	Trial burn; 0.34 kg/h PCB + 18.7 kg PCDM* added
Kumla, Sweden	1983	15	Old Technology
2 plants in The Netherlands	1987	1.2-2.3	
		27	Old Technology
Rechem International, Pontypool, United Kingdom	1987	0.08	ca. 4 000 kg PCB/d; new flue gas cleaning installed
Rechem International, Fawley, United Kingdom	1990	0.06-0.15	Normal operation

The German TA Luft (an ordinance for industrial plants that need special surveillance with respect to stack emissions) has a requirement for minimization of dioxins emitted from such plants. In this context two groups of industrial emitters need special attention:

- Plants with high dioxin emissions (> 1 ng TEQ/m^3) and especially when the emissions may have an direct impact to the neighbourhood (e.g. plants do not have high stacks or diffuse outlets through the roof of the buildings can occur).
- Plants with high emissions of dioxins due to large volumes emitted and subsequently causing a potential impact on the terrestrial food-chain and increasing human exposure.

The state of Northrhine Westfalia (Germany) has initiated a program to evaluate 42 priority industrial facilities with potentially relevant dioxin emissions to the air. The program includes analyses of gaseous emissions from remelting plants and foundries (total of 28 plants), plants for wood combustion (5 plants), for melting, sintering, raw-iron and non-ferrous-raw material manufacturing, chipboard manufacture and manufacture of compounds using chemical processes with chlorine involved (wood preservatives, distillation of waste oil, bleaching of cotton and threads). So far, dioxin emissions < 0.1 ng I-TEQ/m^3 were found for most of the plants investigated. However, facilities with emissions > 1 ng I-TEQ/m^3 were identified, too (Table 2).

Table 2: First results of the dioxin program in Northrhine Westfalia - Plants with emissions more than 1 ng I-TEQ/ m^3 (mean value of three measurements); (x) = retrofitting started or finished
( ) = new measurements after installation of primary or secondary measures

Type of Plant	Concentration (ng I-TEQ/m^3)		Emission Mass Stream (mg I-TEQ/h)
Hot briquetting for recycling materials	70	(x)	3.7
Sintering plant for recycling materials	46.7	(x)	13
Sintering plant for iron-ore	43.2	(0.7-2.0)	29
Rolling mill for recycling materials	20.8	(x)	1.04
Sintering plant for iron-ore	11.6	(1.9-3.5)	5.8
Tin plant	5.9	(x)	0.09
Combustion of waste wood, 1 MW	5.8	(0.6)	0.009
Lead-tin melting plant	2.7		0.04
Sintering plant or iron-ore	2.4		1.6
Sintering plant for iron-ore	1.9		2
Recycling of metal turnings	1.1		0.038
Sum			56.3
For comparison:			
Municipal waste incinerator	5		0.5
Modern municipal waste incinerator	0.1		0.01

Among the facilities with emissions far below 0.1 ng I-TEQ/m^3 were blast furnaces, aluminium melting plants, zinc melting plants, a vinyl chloride manufacture, a crematory with biofilter, glass industry, and facilities for combustion of bark and paper.

3.2 Sewage Sludge and Compost

PCDD/PCDF analyses of German sewage sludges indicate a trend for decreasing levels for the last six years. Analytical data on dioxin levels in sewage sludges obtained from 30 and 28 sewer plants, resp., in the area of Frankfurt/Germany (densely populated, industrialized) have been published (see Table 3). In most cases PCDF concentrations were about half of the PCDD concentrations. In 1991 two out of 30 sewage sludge samples showed levels above the limit value of 100 ng I-TEQ/kg d.m. set by the German Sewage Sludge Ordinance; in 1992 no concentrations above the limit value was reported.

Table 3: PCDD/PCDF levels in sewage sludges, data from two subsequent years, same sewer plants (Sachs-Paulus 1992)

	August 1991	March 1992
Number of samples	30	28
Minimum	18 ng TEQ/kg d.m.	9 ng TEQ/kg d.m.
Maximum	144 ng TEQ/kg d.m. (620 ng TEQ/kg d.m.)	63 ng TEQ/kg d.m.
Mean	39 ng TEQ/kg d.m. [1]	24 ng TEQ/kg d.m.
Median	32 ng TEQ/kg d.m. [1]	23 ng TEQ/kg d.m.
Samples TEQ > 100 ng/kg d.m.	2	0
Samples TEQ > 50 ng/kg d.m.	8	1

[1] = results without the extreme value of one sewage sludge plant

Figure 1 gives the distribution frequency of PCDD/PCDF (in TEQ) from 101 bio-compost samples. Most sample levels were between 7.49 and 17.5 ng TEQ/kg d.m.; the median being 11.3 ng TEQ/kg dry matter (Fiedler et al. 1994).

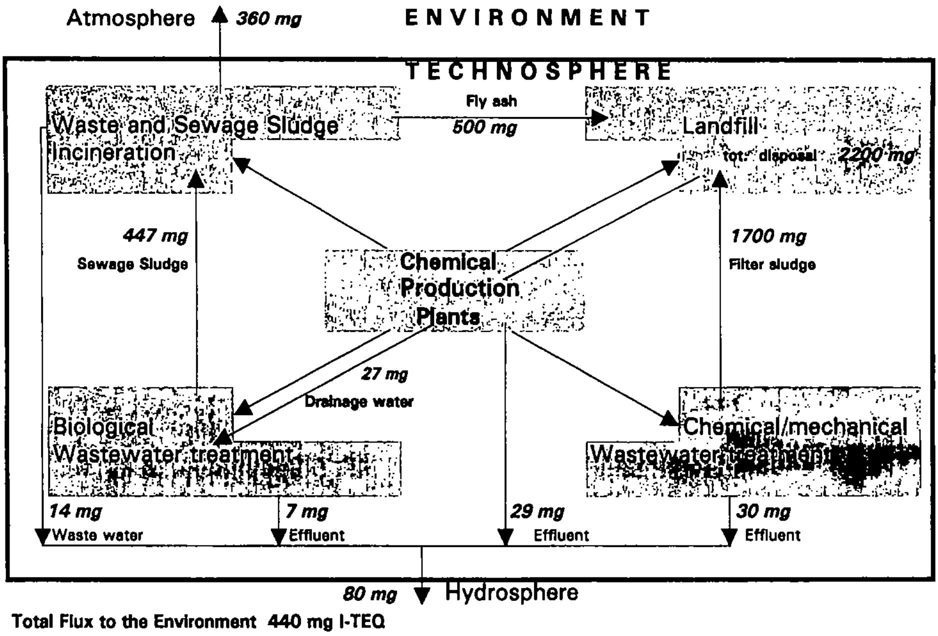

Figure 2: Dioxin mass balance of a chemical manufacturing site (PCDD/PCDF emissions in mg I-TEQ per year)

Presently, the HWI is equipped with activated carbon filter. The emissions to the atmosphere - data for 1993 - will be reduced to 21 mg/yr. in the future when a dioxin catalyst will be installed at the hazardous waste incinerator.

5 Environmental Air Concentrations and Impact on Soil

Ambient air concentrations found in Germany can be summarized as follows (see Table 4) (BGA 1993):

Table 4: Annual mean values of PCDD/PCDF for ambient air concentration and deposition in Germany (BGA 1993)

Description of Location	Ambient Air Concentration ($pg TEQ/m^3$)	Deposition ($pg TEQ/m^2 \cdot d$)
Rural area	0.025-0.070	5-20
Urban area	0.070-0.350	10-85
Close to point source	0.350-1.600	up to 1,000

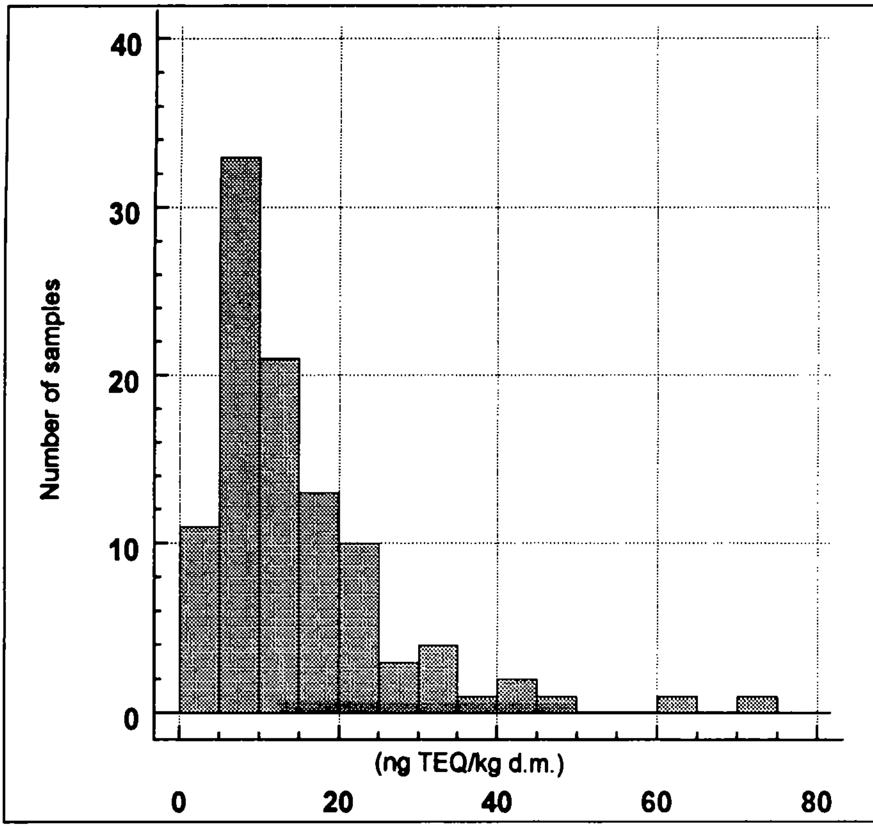

Figure 1: Distribution of PCDD/PCDF concentrations in bio-compost. Concentrations in (ng I-TEQ/kg d.m.); 101 samples analyzed

4 Mass Balance of a Chemical Manufacturing Site

A dioxin mass balance has been performed for a chemical manufacturer's production site in Germany (Wacker Chemie GmbH 1994). Figure 2 gives an overview on the dioxin flows and outputs of this site. Main products of the chemical company are: PVC (largest producer in Germany), silicone and silanes, rubber, sealants, high purity silicium (microchip production), polyvinylacetate polymers (dispersion medium for dyes, adhesives, paper, textiles), organic intermediates (catalysts, pharmaceuticals, pesticides, and dye stuffs). In total approx. 3,000 chemicals enter or leave the various plants or are produced on this site. As can be seen from Figure 2 PCDD/PCDF emissions can be effectively controlled and monitored also for a large chemical production site when appropriate measure are installed.

Besides sediments, soils are the ultimate sinks for persistent chemicals such as heavy metals and persistent organic compounds, e.g. PCDD/PCDF. Persistence means that transformation processes do not play an important role; in other words, biodegradation by microorganisms, hydrolysis, and photolysis do not affect the molecular structure of the molecule. Thus, any new entry of 2,3,7,8-substituted PCDD/PCDF (expressed as I-TEQ) will increase the present soil concentration. By use of a simple model four exposure scenarios - atmospheric deposition, application of sewage sludge, compost, and pesticides - were run to calculate the number of years that are needed to cause an increase of 1 ng I-TEQ in soil. It is assumed that photolytic and biological degradation are negligible for 2,3,7,8-substituted PCDD/PCDF. The basic assumptions and the results are given in Table 5.

Table 5: Exposure scenarios for dioxins in soils (Density of soil = 1.4 g/cm^3)

Matrix	PCDD/PCDF Concentration Use Pattern	Depth of Application/Mixing	Years Needed to Cause an Increase of 1 ng TEQ in Soil
Deposition	10 pg $TEQ/m^2 \cdot day$	30 cm	115
		10 cm	38.5
	30 pg $TEQ/m^2 \cdot day$	30 cm	38.5
		10 cm	12.8
Sewage Sludge	50 ng TEQ/kg d.m. 5 tons d.m./ha in 3 yrs.	30 cm	10
Compost	14 ng TEQ/kg d.m. 10 tons d.m./ha per yr.	30 cm	30.3
2,4,5-T Pesticide	2 mg TEQ/kg 2,4,5-T applied on 1,000 m^2	30 cm	2.5 ng per application

The dioxin levels in sewage and compost do not cause any hazard to cattle and humans, especially as the transfer factors of PCDD/PCDF from soil to plants are $\ll 0.1$. However, in terms of soil protection any additional impact with PCDD/PCDF *via* intentional application of dioxin-containing materials has to be evaluated carefully. As a further consequence, dioxin levels in sewage sludge and compost should be minimized by controlling the input.

6 References

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