Dioxin Mass Balance for the City of Hamburg, Germany: Part 1: Objective of the Study and Emission Inventory

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1 ABSTRACT

Sources and reservoirs of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/PCDF) were quantified for the city of Hamburg, Germany. For the year 1992, annual fluxes and emission inventories of PCDD/PCDF were estimated for combustion sources. The total emissions were in agreement with the total deposition flux. However, the results of such a „snapshot" do not implicate that all mass balances should inquire that emissions equal deposition for any given region. Measures taken during the last years in Hamburg have already markedly reduced emissions of PCDD/PCDF into the environment. To further minimize dioxin exposure, national and international measures have to be taken.

Keywords: *Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF), emission inventory, fluxes*

2 INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/PCDF) are unwanted by-products of many chemical industrial and combustion processes. The known toxicity and persistence in the environment of some congeners has resulted in many efforts worldwide a) to identify processes which are suspect to generate PCDD/PCDF, b) to determine levels of PCDD/PCDF in environmental compartments (*e.g.* in soil, sediments, and air), in products (*e.g.* in chemicals, paper, other consumer products, and food), in residues and emissions (*e.g.* municipal waste, fly ash, flue gases of incinerators, sewage sludge, *etc.*), c) to understand transport and distribution of PCDD/PCDF, and d) to determine human exposure. In addition, technological measures were developed to minimize dioxin emissions and exposure. For the first time, fluxes of PCDD/PCDF should be evaluated on a regional scale. Thus, the joint project „Dioxin Mass Balance for the City of Hamburg" was performed.

With a population of 1.65 million inhabitants Hamburg is the second largest city in Germany; in addition, Hamburg is a federal state, too. Its area is 755 km^2. Hamburg has a highly urban industrial infrastructure with 2,200 inhabitants/km^2 (for comparison: German average = 228 inhabitants/km^2).

Hamburg has a long „dioxin" history including a former 2,4,5-T production site, the landfill „Georgswerder" and others are contaminated with PCDD/PCDF; in addition, sediments from the harbour and the river Elbe are contaminated with dioxins. Hamburg has several combustion sources (two municipal waste incinerators, one hazardous waste incinerator, steel works, and non-ferrous metal industry).

The objective of the dioxin mass balance for Hamburg was to evaluate origin or cause of PCDD/PCDF loads and reservoirs in the city, to identify average/characteristic levels and fluxes of PCDD/PCDF, to establish trends of environmental concentrations, and to calculate the daily intake of PCDD/PCDF by a typical person living in Hamburg (for results, see Wesp *et al.* 1996). Finally, measures and recommendations should be given to reduce emissions of PCDD/PCDF into the environment and to minimize human exposure (for details see Friesel *et al.* 1996)

So far, no dioxin mass balance exists for an urban region such as the city of Hamburg. Existing calculations were either restricted to emissions of PCDD/PCDF to air as for Germany or the federal states of Baden-Württemberg and Berlin (Wintermeyer and Rotard 1994, Hagenmaier and Krauß 1993, Hutzinger and Fiedler 1993, Jager *et al.* 1992). So far, reservoirs of PCDD/PCDF have not been quantified in detail for any region. Correlations between PCDD/ PCDF concentrations in environmental compartments and consumer goods with human exposure were not performed on such broad basis. In this paper, we report the results of the emission inventory for Hamburg in the year 1992.

3 EXPERIMENTAL

Since 1983, more than 800 congener-specific dioxin analyses were performed in Hamburg to determine levels of PCDD/PCDF in water, soil, and air. Emissions and residues from industrial processes (*e.g.* waste incineration, composting, sewer plants (POTWs), *etc.*), landfills, and contaminated sites were analyzed for PCDD/PCDF. Finally, special monitoring programs were established to determine dioxin concentrations in vegetables, foodstuffs, meat, and cow milk (FHH 1991, FHH 1993). The number and quality of dioxin results is unique for any defined region in Germany. All concentrations of PCDD/PCDF were given in I-TEQ (International Toxicity Equivalents).

Almost complete statistical data were obtained for the year 1992; whenever possible, newer data were incorporated into the dioxin balance for Hamburg. Although many PCDD/PCDF analyses did exist for the Hamburg region, external data had to be used, too: *e.g.* there was no Hamburg-specific dioxin data available for the concentration of PCDD/PCDF in municipal solid waste, in household effluents, *etc.* In such cases, an expert meeting was held to determine the appropriate data by checking for plausibility and representativeness.

4 RESULTS

4.1 PCDD/PCDF Emission from Combustion Sources in Hamburg

For Hamburg, PCDD/PCDF emissions to the air are predominantly from industrial and commercial activities (production/manufacture and finishing processes), domestic activities (home heating), waste incineration, and traffic (automobiles). According to our evaluation, in 1992 a total of 6.5 g I-TEQ were emitted from identified and quantified sources in Hamburg. Table 1 gives an overview on the combustion sources and the annual amount of PCDD/PCDF released from these sources to the atmosphere.

Table 1: PCDD/PCDF emissions to the air from combustion sources in Hamburg

Source	Flux (mg I-TEQ/a)
Stationary Sources	
Industry:	
Copper industry	1,200
Aluminium industry	8
Iron and steel manufacture	166
Petrochemical industry	0.009
Smoke houses (smoked fish and meat)	8
Others:	
Crematories	4-21
Generation of Power:	
Power plants (fossil fuels)	69
Industrial wood combustion	150
Combustion of sewer gas	14
Waste disposal in Hamburg	
Municipal waste incineration	3,913
Hazardous waste incineration	560
Subtotal Stationary Sources	***6,092-6,109***
Diffuse Sources	
Traffic	
Automobiles	250
Households:	
Home heating	70-340
Accidental fires in homes	8
Subtotal Diffuse Sources	***328-598***
Sum of All Known Sources	**6,420-6,707**

In the year 1992, incineration of municipal solid and hazardous waste was the major sector (industry) to emit PCDD/PCDF into the air; an annual flux of 4.5 g I-TEQ was attributed to this category (see Table 1). Retrofitting of the combustion facilities, shut-down of one old incinerator and installation of a new incinerator resulted in a reduction of more than 95 % for the year 1995 (total emissions from waste incineration: less than 0.2 g I-TEQ/a). Emissions from thermal industrial processes, especially from a copper plant and to a minor extent from iron and steel production, generation of

aluminium, and smoke-houses were also of importance (for discussion of reduction measures, see Friesel *et al.* 1996). The contribution from generation of energy - fossil fuel power plants and combustion of sewer gas - was low when compared to the total amount of PCDD/PCDF emitted. Relatively large uncertainties exist for the estimate of PCDD/PCDF emissions from home heating. Our best estimate for 1992 was between 70 and 340 mg I-TEQ/a.

4.2 Deposition

The annual mean of PCDD/PCDF levels in the air of Hamburg were determined to be 50 fg I-TEQ/m^3 and thus, in the range commonly found in German cities. The annual mean takes into consideration that in Hamburg as well as in other regions, PCDD/PCDF levels in air are higher during the winter months and lower during summer (Fiedler 1996, Hiester *et al.* 1995). Assuming a mixing layer of 1,000 m above Hamburg (as is done in environmental fate models), an amount of 0.04 g I-TEQ is present in the air column at any time. Multiplication of the air volume with the area of Hamburg and the mean wind speed (4.2 m/s) and assuming that the dioxin concentrations are similar inside the city limits and outside, a total amount of 250 g I-TEQ was transported through Hamburg in the year 1992.

For Hamburg, a mean deposition rate of 10 pg I-TEQ/(m^2·d) was determined for the year 1992. Thus, a total of 2.8 g I-TEQ was being deposited on the city's area in 1992. Compared to the amount of 250 g I-TEQ present in the air, roughly 1 % of the total PCDD/PCDF was eliminated from the atmosphere by particulate deposition. Recent results by Wallenhorst *et al.* (1995) showed that in Baden-Württemberg (Germany) the distribution of PCDD/PCDF between the particulate phase and the gaseous phase is about 1:1 when expressed as I-TEQ. Thus, it can be assumed that the combined particulate and gaseous deposition in 1992 was 5.6 g I-TEQ. Astonishingly, this number is in agreement with the total of 6.5 g I-TEQ/a emitted from all known combustion sources in Hamburg. Table 2 summarizes major results on the concentrations of PCDD/PCDF in the air of Hamburg.

Table 2: Summary of PCDD/PCDF in the air of Hamburg for the year 1992

Flux/Reservoir	Load		
Stationary mass:	40	mg I-TEQ	
Maximum horizontal flux with aerial transport	250,000	mg I-TEQ/a	
Emissions from known sources	6,500	mg I-TEQ/a	
Deposition:	2,800	mg I-TEQ/a	particulate deposit
	2,800	mg I-TEQ/a	gaseous depositio
Total:	5,600	mg I-TEQ/a	
Percentage of deposition from horizontal flux	2.2		
Percentage of Hamburg sources to horizontal flux	2.6		

5 CONCLUSIONS

The dioxin mass balance for the city of Hamburg is the first attempt to exhaustively characterize and determine inventories and fluxes for all environmental compartments for organic compounds (FHH 1995, Friesel *et al.* 1996, Lau *et al.* 1996, Wesp *et al.* 1996). So far, such mass balances did only exist for some heavy metals and nutrients (phosphorus and carbon) (Baccini and Brunner 1991). The emission inventory for PCDD/PCDF from combustion sources gave plausible and consistent results for a multitude of sources, so that the uncertainty of our estimation is relatively small. As a result, due to installation of emission control devices, technical measures, and restructuring of the industries, PCDD/PCDF emissions from thermal industrial sources in 1995 were substantially reduced compared to 1992 (for a more detailed discussion, see Friesel *et al.* 1996).

Within the category of waste incineration, minimization potentials have been exhaustively used by installing sophisticated flue gas cleaning devices and replacing existing plants by new ones. PCDD/PCDF emissions from automobiles were due to the presence of halogenated scavengers in leaded fuel. Assuming a further decrease in the use of leaded gasoline and increasing numbers of cars equipped with catalysts, a further reduction of dioxin emissions from traffic can be postulated for Hamburg, too. Based on our evaluation, within the industrial sources there is still a potential to further reduce dioxin emissions. These reductions can only be realized by cost-extensive technological changes, *e.g.* smaller stack volumes.

A high degree of uncertainty still exists for the estimate of the contribution from private heating. Although there exists an abundance of PCDD/PCDF emission data for incineration of wood and fewer of coal and oil, the number of installations and the frequency of using the heating systems remains unknown (*e.g.* type of fuel burnt, is combustion of fossil fuels in private ovens just for heating during winter or also for generation of hot water and other energy?). Due to such lack of information, we came to the conclusion that additional dioxin measurements even of a large number of installations will not give further insight to more precisely calculate the annual load of PCDD/PCDF released from this source category.

We found an excellent agreement on the amount of PCDD/PCDF being emitted from known sources in Hamburg (6.5 g I-TEQ/a) and deposition (5.6 g I-TEQ/a) for the year 1992. It should be noted however, that both numbers are only a small percentage of the total dioxin mass transported through Hamburg during one year (250 g I-TEQ). As since 1992, measures were undertaken to further reduce dioxin emissions to the air (see Friesel *et al.* 1996) the annual emissions from Hamburg's combustion sources will be reduced to less than 1.5 g I-TEQ; the deposition, however, did not decrease the same way. Thus, it cannot be concluded that for mass balances, emissions of PCDD/PCDF have to equal deposition as such consideration neglect aspects such as long-range transport, meteorology, potential transformation processes in the atmosphere, *etc.* As a consequence, applying simple models using air columns above a given area is not appropriate and will lead to the assumption that most of the dioxin sources are still unknown (Travis and Hattemer-Frey 1990, Harrad and Jones 1992, Wintermeyer and Rotard 1994, Thomas and Spiro 1995). In general, these findings underline the importance of long-range transport of persistent compounds and the demand for further research on better understanding transport and behaviour phenomena in the atmosphere.

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