Investigations on Potential Sources of Polychlorinated Dibenzodioxins and Dibenzofurans in Sewage Sludges

W. Klöpffer, R. Gihr, G. Rippen and H. Partscht
Battelle-Institut e.V., 6000 Frankfurt am Main 90, Am Römerhof 35
U. Stoll and J. Müller
Lahmeyer International, 6000 Frankfurt am Main 71, Lyoner Straße 22

Abstract:

In 1989 the mean value of concentration of PCDD/F in 72 Federal German sewage sludge samples was about 20 µg/kg dry matter (range: 1.7 to 150 µg/kg dry matter), which corresponds to an annual amount of 50 kg PCDD/F introduced into the sewage sludge (for comparison: about 125 kg PCDD/F in 1986). Formation and direct introduction of PCDD/F into sewage treatment plants and its introduction into sewage sludge from the atmosphere and from various industrial sources was examined with respect to their quantitative relevance to sewage sludge.

Introduction:

Analyses of sewage sludges from a major number of sewage treatment plants made by Hagenmaier et al. since 1986 showed unexpectedly high PCDD/F peak values of up to about 300 µg/kg dry matter and an arithmetic mean of about 1/10 of the peak value; as a rule, the concentration of PCDD is higher than that of PCDF, the completely chlorinated OCDD predominating among the PCDDs. These results and the combination of high toxicity and persistence that is characteristic of this class of substances, but relatively rare for environmental chemicals, give high priority to the question about the sources of PCDD/Fs in sewage sludges.

The objective of the reported work was to determine and approximately quantify the most important sources of the PCDD/Fs detected in sewage sludges. The results are to be used as the basis for measures to reduce the amounts introduced into the sewage sludge. The following priorities were defined for the investigations:

1) Obtain information on the role of pentachlorophenol (PCP) and its derivatives, a group of substances which are particularly highly polluted with OCDDs.

2) Assess the contributions by the paper and cellulose industry and by its products.

3) Research additional sources that have been given less attention so far.

The work was based primarily on discussions with experts, contacts with industry, and published or "grey" literature. In addition, chemical analyses of environmental samples and

chemical products were made to a limited extent, as far as they appeared necessary for rapid verification or falsification of working hypotheses.

Battelle-Institut e.V., Frankfurt am Main, had overall responsibility for the work which was carried out in the period from May 1989 to June 1990 in cooperation with Lahmeyer International, also in Frankfurt am Main.

Results and Discussion:

Preliminary Assessment of the Most Important Sources and Paths:

The annual sewage sludge volume generated by municipal sewage disposal is approximately 50 million m^3, which corresponds to 2.5 million t dry matter.

The mean value of PCDD/F concentration in sewage sludge samples (n = 72) determined in 1989 in Hesse, Rhineland-Palatinate, Lower Saxony and Schleswig-Holstein was about 20 µg/kg dry matter (range: 1.7 to 150 µg/kg dry matter). Hagenmaier, on the other hand, found a mean value of 50 µg PCDD/F/kg dry matter for the sewage sludge samples from the entire Federal Republic of Germany analysed in 1986.

The mean total PCDD/F amount contained in the municipal sewage sludge produced in the entire Federal Republic of Germany thus results to be about 50 kg on the basis of recent values and 125 kg related to the values of Hagenmaier.

The PCDD/F amounts introduced into the environment or into the sewage sludge were assessed for the following paths and industrial sources:

1) PCDD/F amounts introduced via the atmosphere (dry and moist deposition)

2) Formation and introduction of PCDD/Fs into the sewage treatment plant:
   a) Biogenously from chlorophenols
   b) From PCP in the presence of hypochlorite
   c) Via phosphate elimination with Fe and Al salts, produced from scrap
   d) Formation of S analogues to PCDD/F from, e.g., pentachlorothiophenol

3) Introduction of PCDD/F from various industrial sources:
   a) Tank truck cleaning
   b) Textile and leather industry
   c) Metal industry
   d) Imported cooling lubricants (mixable with water)
   e) Oils for processing metals
   f) Metal degreasing
   g) Hospital refuse incinerating plants
   h) Dry cleaning
   i) Automobiles (tyres, exhaust gases)
   k) Refuse incinerating plants
   l) Construction chemistry (wood preservatives)

EMISSION FACTORS OF PCDD AND PCDF FOR ROAD VEHICLES OBTAINED BY A TUNNEL EXPERIMENT

S. Larssen, E.M. Brevik and M. Oehme
Norwegian Institute for Air Research, P.O. Box 64, N-2001 Lillestrøm, Norway

INTRODUCTION

In recent years different studies have been carried out to estimate the emission factors of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) using measurements performed in car exhaust test laboratories [1]. However, such results can always be questioned due to the following reasons. The small number of cars tested can never truly represent the average emission from an entire car fleet and the employed driving cycle may not necessarily represent real driving conditions.

Road tunnels represent an opportunity to obtain exhaust emission factors which are representative for the car population and the various traffic conditions that prevail in the tunnel. Especially in longitudinally ventilated tunnels the parameters necessary to calculate emission factors can be fairly accurately determined. Based on the measurements in a road tunnel in Oslo, Norway the emission factors for PCDD/PCDF were calculated for different traffic situations based on an average daily traffic of 8'000-14'000 cars.

EXPERIMENTAL

The methodology for the calculation of the PCDD/PCDF emission factors was as follows: PCDD/PCDF concentrations were measured at the inlet and outlet of each tunnel tube. Simultaneous measurements of traffic parameters such as traffic density, speed and vehicle composition (light duty and heavy duty) as well as the average air flux through the tunnel were also carried out. This allowed the calculation of emission factors using the following equation:

$$q = \frac{\Delta C \cdot V \cdot A}{t \cdot L}$$

where: q: average emission factor (g/km) representing the traffic between the two sampling points.
ΔC: concentration difference (g/m^3) between the two sampling points.
V: average air flux (m/s) between the two sampling points.
A: average cross sectional area of the tube (m^2).
t: traffic density (units/s).
L: distance between the two sampling points (km).

By performing measurements at times with different heavy duty diesel truck (HDDT) percentage of the total traffic (e.g workdays vs. weekend), it is possible to calculate the emission factors for light duty (gasoline) vehicles (LDV) and HDDT separately.

All measurements were carried out during the period 20 April to 7 May, 1989 in the Vålerenga tunnel in Oslo, Norway, which consists of two parallel tubes, one for each traffic direction. The north bound tunnel has an average incline of ca 3.5%, a cross-sectional area of 78 m^2 and 3 lanes (southbound: 3.5% decline, 69 m^2, 2 lanes). Further details about traffic density, average speed and percentage of HDDT traffic are given in Table I. PCDD/PCDF were collected by a high volume sampler equipped with a glass fibre filter of 142 mm ø and two polyurethane foam plugs in series. More details about the sampling method are given in [2]. Sampling was carried out during daytime traffic (0800-2000 hrs) for totally 14-24 hrs spread over two working days or saturday and sunday. Samples were simultaneously collected at the tube in- and outlets. The total sample volume varied between 300-500 m^3 and the particle load between 130-413 mg. In addition to PCDD/PCDF, continuous monitoring of CO, NO_x, NO_2 was carried out. The traffic volume, speed and vehicle length were detected continuously by means of inductive detectors installed in each traffic lane. Vehicles over 7 m length were classified as HDDT.

Quantification of PCDD/PCDF was carried out according to the method described in [2] using the following modifications. ^{13}C-marked 2,3,7,8-chlorine substituted isomers were used as recovery and quantification standards for sampling and analysis. An upscale of the clean-up columns by a factor of 3 was employed. Recovery of the added isotope-marked congeners was in average 50-70%. The detection limits were 0.02 pg/m^3 or better included 2,3,7,8-TCDD. The determined PCDD/PCDF levels were calculated as 2,3,7,8-tetrachlorodibenzo-p-dioxin equivalents according to the Nordic model [3].

The air flux through the tunnel was measured by a tracer gas technique. Sulfur hexafluoride (SF_6) was released at a controlled and measured rate at the tunnel inlet and the tracer gas concentration determined over the tunnel

cross section near the outlet. The average air velocity was calculated according to the equation:

$$V = \frac{Q_{SF_6}}{C_{SF_6} A}$$

where: V: average air velocity (m/s) between the release and measurement cross sections.
A: cross sectional area of the tunnel (m^2).
Q_{SF_6}: tracer gas release rate (g/s).
C_{SF_6}: average tracer gas concentration (g/m^3) at the measurement cross section.

RESULTS AND DISCUSSION

As can be seen from Table I and II, the collected samples allowed the calculation of 2,3,7,8-TEQ emission factors for different traffic situations. The largest emission factors were obtained during workdays in the inclining tunnel tube with a free flowing traffic at about 60 km/h. The tetra- and pentachloro-CDF/CDD as well as the hexachloro-CDF isomers contributed most to the observed differences. The PCDD/PCDF level at the inlet of the tubes was little influenced by the traffic situation and was in the order of 0.1 pg/m^3 2,3,7,8-TEQ.

Table I: Traffic data and calculated 2,3,7,8-TEQ emission factors obtained by the tunnel measurements. The average values are determined on basis of the given data. 2,3,7,8-TEQ values according to the Nordic model.

Parameter	Northbound tube		Southbound tube	
	Inlet	Outlet	Inlet	Outlet
Daily average no. of cars [% of HDDT in ()]				
Workdays	14'170 (14.8)		11'930 (19.0)	
Saturdays	10'310 (3.7)		8'370 (5.7)	
Sundays	12'680 (6.2)		11'150 (8.2)	
Average speed [km/h]	59		68	
Measured traffic density [veh./s], % HDDT in ()				
Workdays	0.28 (15)		0.176 (18)	
Saturday/Sundays	0.175 (3.5)		0.070 (5.5)	
2,3,7,8-TEQ levels [pg/m^3]				
Workdays	0.1	1.0	0.13	0.23
Saturday/Sundays	0.09	0.55	0.10	0.13
2,3,7,8-TEQ emission factors [ng/km]				
Workdays	1.9		0.16	
Saturday/Sundays	0.88		0.075	

Compared to the weekends the percentage of HDDT was a factor of 3-4 higher on workdays which also resulted in a substantially increased emission of PCDD/-PCDF. This difference allowed the estimation of the 2,3,7,8-TEQ emissions factors for light duty (LDV, about 95% gasoline powered) and heavy duty diesel vehicles (HDDT) by extrapolating the results to 0 and 100% HDDT respectively. As a control measure the emission factors for CO and NO_x were calculated as well. The obtained CO and NO_x factors shown in Table II for both vehicle categories are reasonable compared to literature values representative for the current Norwegian car fleet [4]. The 2,3,7,8-TEQ emission factors for LDV were within the same range as reported earlier for single car experiments [1]. A rather large difference was found for the two traffic situations in the tunnel. The values obtained for HDDT which exceeded those for LDV by a factor of 20-30 were quite surprising. Very little is known about the PCDD/-PCDF emission from diesel engines.

Table II: Emission factors of 2,3,7,8-TEQ, CO and NO_x for LDV and HDDT in the northbound (3.5% incline, 60 km/h) and southbound tube (3.5% decline, 70 km/h).

Parameter		Northbound		Southbound	
		LDV	HDDT	LDV	HDDT
2,3,7,8-TEQ	ng/km	0.5	9.5	0.04	1.3
CO	g/km	10	10	5	5
NO_x	g/km	3.5	36	0.5	1.3

In 1985, the total traffic in Norway corresponded to about 19.4 10^9 km/year for LDV and 1.7 10^9 km/year for HDDT. Using as a first estimate the average emissions factors given in Table II, the annual 2,3,7,8-TEQ emissions from car traffic in Norway were assessed to 5.2 g from LDV and 9.2 g from HDDT.

REFERENCES

[1] Marklund, S., Rappe, C., Tysklind, M. and Egebäck, K.-E., Chemosphere 16, 29-36 (1987).

[2] Oehme, M., Manø, S., Mikalsen, A. and Kirschmer, P. Chemosphere 15, 607-617 (1986).

[3] Ahlborg, U. G., Håkonsson, H., Waern, F. and Hanberg, A. (1988) Nordisk dioxinriskbedömning (with English summary). Nordic Council of Ministers, Miljörapport 1988:7, NORD 49:5-111, Copenhagen.

[4] Egglestone, E.S., Gorissen, H., Joumard, R., Rijkeboer, R.C., Samaras, Z. and Zierock, K.H. Summary Report of the CORINAIR Working Group on Emission Factors for Calculating 1985 Emissions from Road traffic. Berlin, Envicon, Draft Final report, December 1988.