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Concentrations of Polychlorinated Dibenzo-p-Dioxins (PCDD) and Dibenzofurans (PCDF) in Urban Runoff and Household Wastewaters

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Abstract

Urban runoff and household wastewater samples were analysed for PCDD/F. The concentrations in street runoff lay between 1 and 11 pg TEQ/L. A roof runoff sample was less contaminated (< 1.7 pg TEQ/L), with levels at most a factor of 2 higher than in a parallel rain water sample. Household wastewater showed higher PCDD/F concentrations of up to 14 pg TEQ/L. The homolog profile agreed well with the profile found in sewage sludge samples. Washing machine effluent is a major source of PCDD/F in household wastewater. PCDD/F were also quantified in shower water.

Keywords: PCDD/F, Street Runoff, Roof Runoff, Household Wastewater, Sewage Sludge, Shower Water, Washing Machine Effluent

Introduction

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) are persistent, lipophilic and, depending on the chlorine substitution, toxic compounds that accumulate in different environmental compartments. An ubiquitous contamination of sewage sludge with these compounds has been reported [1,2,3], and it has been shown that the agricultural use of sewage sludge as a fertiliser can cause an accumulation of PCDD/F in soils [4]. Very similar PCDD/F homolog profiles have been observed in sewage sludge samples collected in municipal wastewater treatment plants (MWTP) across Germany [5]. The similarity between this typical sludge profile and the profile measured in technical pentachlorophenol (PCP) led to the hypothesis that the use of technical products containing PCP in different industries was the main source of the PCDD/F in sewage sludge [6]. However, PCDD/F contamination displaying the same profile was also found in sewage sludge with no industrial inputs and in isolated household wastewater treatment systems [5,7]. Attempts have been made to resolve this contradiction and identify the PCDD/F sources in detail [8,9], with limited success. In an earlier paper we provided evidence indicating that household wastewater and not surface runoff contributes the majority of the PCDD/F in sewage sludge [10]. We more recently proposed that a large portion of the PCDD/F originates in textiles, and that the PCDD/F are washed out of the textiles in the washing machine as well as being washed off of human skin during bathing [11]. In this paper we provide full isomer specific concentration data on a range of the samples analysed in this work to assist in future efforts to quantify PCDD/F fluxes in municipal wastewater. Results are presented for urban street runoff, storm water sediment trap sediments, sewer sediments and household wastewater collected in Bayreuth, a small city of 70,000 in northeastern Bavaria, as well as for washing machine effluent and shower water.

Analytical Methods

The aqueous and particulate phases of runoff water and household wastewater were separated by filtration. The filtrate was extracted three times with toluene (20% of the sample volume) in a separatory funnel. The filters were extracted in toluene for 24 hours using a Soxhlet apparatus as were the sediment samples following drying at 75°C. An internal standard mixture containing 11 ^{13}C-labelled and one ^{37}Cl-labelled 2,3,7,8-substituted PCDD/F congeners in toluene was added to either the solvent or the sample prior to extraction of all samples.

A solid phase extraction (SPE) method was developed for extracting the washing machine effluent and shower water. PCDD/F from unfiltered samples of up to 2000 mL were enriched on 26 mm cartridges containing octadecyl silane (C_{18}) bonded to a silica substrate (VARIAN MEGA BOND ELUT; 10 g sorbent). The sorbent was conditioned with 20 mL n-hexane, 20 mL dichloromethane, 20 mL methanol and 300 mL aqua bidest under low vacuum. The samples were drawn through the C_{18}-sorbent at a maximum flow rate of 50 mL/min by applying a mild vacuum. After the enrichment the remaining water on the sorbent was removed by sucking air through for 5 minutes and subsequently allowing the cartridge to stand for 2 days at room temperature. The internal standard mixture was then added to the top of the cartridge and the PCDD/F were eluted with 50 mL of toluene. The solvent was transferred directly to the first column used for the sample cleanup. The extraction efficiency was tested with five laundry wastewater samples which were divided in two equal parts. One half was extracted with the SPE-method, while the extraction of the parallel sample was done by liquid/liquid extraction with toluene. The PCDD/F concentrations were compared for each homolog of the five sample pairs. In comparison to the liquid/liquid extraction with toluene (=100%) the average SPE efficiency lay between 97% and 130% for all PCDD/F homologs. The SPE method saved time and required only 5% of the solvent used in liquid/liquid extraction.

The cleanup and HRGC/HRMS analysis of all samples were as described in [12]. The 2,3,7,8-Cl_4DD toxicity equivalents (TEQ values) were calculated using the NATO-CCMS factors [13].

Results and Discussion

Runoff Water

Street runoff samples were collected at a busy intersection in Bayreuth (more than 16,000 vehicles per day) at the beginning and end of two rain events in July 1991. About 4 L of runoff water were sampled with an automated device developed by the Hydrology Department of the University of Bayreuth and described elsewhere [14]. This device was constructed without a sediment trap to avoid loss of sediment material during sampling. Litres 3 - 6 of a runoff event sampled as "first flush", while the sixth last to third last litres were sampled as "last flush".

The first rain event on July 14 lasted eight hours. The rain intensity was relatively constant over this period (0.3 mm/h - 0.55 mm/h). Table 1 gives the PCDD/F-concentrations of the samples from the beginning and end of this event. On July 26 two more samples were taken at the beginning and end of a runoff event caused by a thunderstorm. In contrast to the first rain event the intensity was very high at the beginning of the storm (3.5 mm/h) and decreased rapidly to zero after 30 minutes. The PCDD/F-concentrations of the second rain event are also shown in Table 1. The concentration values include the aqueous and the particulate phases but in all four cases more than 99.9% of the PCDD/F were adsorbed to the particulate matter.

The PCDD/F concentrations in the runoff from 14.07.91 were approximately constant in both samples (< 2.5 pg TEQ/L in the first flush; < 3.5 pg TEQ/L in the last flush). Only Cl_8DD showed a slight increase at the end of the first event. During the second event the PCDD/F levels decreased by a factor of 5 to 12 (10.2 pg TEQ/L in the first flush; < 1.9 pg TEQ/L in the last flush). This was likely due to changes in the rain intensity and its effect on the cleansing of the street surface. Because PCDD/F are almost completely adsorbed to particulate matter the contaminant flux is determined by the concentration on the particles and the amount of particulate matter resuspended by the runoff. The PCDD/F flux during the first event was likely quite constant since the concentration of particulate matter in the runoff was relatively constant. Some 0.27 g/L were present in the first flush and 0.11g/L in the last flush, where the difference was caused by the absence of sandy material in the last sample. The fine material that is responsible for most of the PCDD/F flux was present in similar quantities in both samples. During the second rain event the flux of particulate matter decreased over time (0.05 g/L in the last flush as opposed to 1.1 g/L in the first flush). This can be attributed to either the decreasing rain intensity and/or a complete cleansing of particulate material from the street during the initial very intensive rain. More detailed studies of other organic compounds (i.e. PAH) with physical-chemical properties similar to PCDD/F showed a strong correlation between the sediment flux and the pollutant flux in street runoff [14,15,16].

Tab. 1: PCDD/F concentrations in urban street runoff from 14.07.91 and 26.07.91 (pg/L)

Street Runoff :	**First Flush, 14.07.91**	**Last Flush, 14.07.91**	**First Flush, 26.07.91**	**Last Flush, 26.07.91**
Σ Cl_4DD	3.5	3	15	1.3
Σ Cl_5DD	14	13	23	6.6
Σ Cl_6DD	29	25	58	13
Σ Cl_7DD	52	60	125	20
Cl_8DD	120	200	420	60
Σ Cl_4DF	20	21	72	16
Σ Cl_5DF	16	15	49	11
Σ Cl_6DF	23	20	69	12
Σ Cl_7DF	22	22	73	11
Cl_8DF	13	16	52	4.3
2,3,7,8-Cl_4DD	< 0.5	< 0.5	< 0.5	< 0.2
1,2,3,7,8-Cl_5DD	< 0.5	< 0.5	< 0.5	< 0.2
1,2,3,4,7,8-Cl_6DD	< 0.5	1.2	< 0.5	< 0.2
1,2,3,6,7,8-Cl_6DD	< 0.5	2.9	19	< 0.2
1,2,3,7,8,9-Cl_6DD	< 0.5	< 0.5	< 0.5	< 0.2
1,2,3,4,6,7,8-Cl_7DD	24	22	68	7
2,3,7,8-Cl_4DF	1.9	1.5	8.2	1.2
1,2,3,4/7,8-Cl_5DF	< 0.5	1.1	5.7	< 0.2
2,3,4,7,8-Cl_5DF	< 0.5	2.0	6.3	1.2
1,2,3,4,7,8/9-Cl_6DF	< 0.5	1.2	5.8	0.9
1,2,3,6,7,8-Cl_6DF	< 0.5	2.9	5.6	0.9
1,2,3,7,8,9-Cl_6DF	< 0.5	< 0.5	< 0.5	< 0.5
2,3,4,6,7,8-Cl_6DF	< 2.5	1.8	12	0.6
1,2,3,4,6,7,8-Cl_7DF	14	14	48	3.2
1,2,3,4,7,8,9-Cl_7DF	1.4	1.0	5.5	0.22
TEQ	< 2.5*/ 1,0**	**< 3.5*/ 2,9****	**< 11*/ 10****	**< 1.9*/ 1.2****

* "<" concentrations included in calculating the TEQs; ** "<" concentrations not included in calculating of TEQs

On 26.07.91 rain water was sampled simultaneously to the street runoff. The rain water contained 21 pg/L Cl_8DD and less of the other PCDD/F-homologs [17]. The PCDD/F-concentrations in the first flush of the street runoff lay up to 20 times higher than in the rain water. In the last flush the difference was only a factor of 2. This indicates that other sources besides rain are responsible for most of the PCDD/F in street runoff. Car engines have been identified as a source of PCDD/F, especially car engines which use leaded fuel [18]. It is likely that residues from car and truck exhaust contribute to the PCDD/F load in street runoff.

Sediment material (< 0.063 mm) from different storm water sediment traps was analysed for PCDD/F. Three locations in Bayreuth with different traffic densities were sampled: Albrecht-Dürer-Str. with >20,000 cars per day; Königsallee with 16,000 cars per day, and Hasenweg with 2,000 cars per day. The concentrations are presented in Table 2.

Tab. 2: PCDD/F in sediments from storm water sediment traps (ng/kg)

Sediments (<0,063mm):	Albrecht-Dürer-Straße	Königsallee	Hasenweg
Σ Cl_4DD	170	38	26
Σ Cl_5DD	210	57	33
Σ Cl_6DD	340	110	87
Σ Cl_7DD	390	320	240
Cl_8DD	860	880	650
Σ Cl_4DF	460	100	88
Σ Cl_5DF	430	83	54
Σ Cl_6DF	330	88	53
Σ Cl_7DF	200	110	68
Cl_8DF	110	73	46
2,3,7,8-Cl_4DD	4.9	< 0.1	< 0.1
1,2,3,7,8-Cl_5DD	12	4.8	3.2
1,2,3,4,7,8-Cl_6DD	23	4.0	2.6
1,2,3,6,7,8-Cl_6DD	45	12	5.0
1,2,3,7,8,9-Cl_6DD	19	6.5	4.2
1,2,3,4,6,7,8-Cl_7DD	150	150	110
2,3,7,8-Cl_4DF	9.0	8.2	7.3
1,2,3,4/7,8-Cl_5DF	5.2	8.0	5.0
2,3,4,7,8-Cl_5DF	7.0	8.3	5.3
1,2,3,4,7,8/9-Cl_6DF	3.5	8.1	5.3
1,2,3,6,7,8-Cl_6DF	3.1	6.1	3.2
1,2,3,7,8,9-Cl_6DF	2.2	1.4	< 0.5
2,3,4,6,7,8-Cl_6DF	1.8	6.2	4.2
1,2,3,4,6,7,8-Cl_7DF	130	64	39
1,2,3,4,7,8,9-Cl_7DF	12	8.5	4.1
TEQ	**29**	**15**	**10**

The results support the hypothesis stated above. The PCDD/F concentrations were highest in sediment material from the Albrecht-Dürer-Straße, the street with the highest traffic density. The homolog profile in this sample showed a larger portion of lower chlorinated PCDD and PCDF in comparison to other samples, an observation that was also made by Schwind for various samples of automobile exhaust [18].

Two samples of roof runoff were collected at the end of October 1991 and analysed for PCDD/F. The concentrations (TEQ: < 1.7 pg/L; Cl_8DD: 50-100 pg/L) were at most a factor of 2 higher than in a parallel rain sample. The homolog profile of roof runoff and rain water agreed well.

The surface areas covered by streets (480 ha) and roofs (500 ha) are nearly equal in Bayreuth. Hence, the higher concentrations measured in street runoff indicate that this is a more important source of PCDD/F to the MWTP than roof runoff.

Sediments (< 0.25 mm) from different parts of the municipal sewer system in Bayreuth were also analysed for PCDD/F. Among the samples were one taken from a sewer servicing only households and surface runoff, one servicing households, surface runoff and industry, one servicing only street runoff, and one from a rain water retention basin. The results are presented in Table 3.

Tab. 3: PCDD/F-concentrations in different sediments (<0.25 mm) from sewer systems (ng/kg)

Sewer Sediment Samples:	Industry, Runoff	Household, Runoff	Runoff	Runoff Basin Sediments
Σ Cl_4DD	5.9	1.5	7.7	10
Σ Cl_5DD	11	6.7	14	14
Σ Cl_6DD	19	33	32	39
Σ Cl_7DD	45	130	82	120
Cl_8DD	220	770	270	410
Σ Cl_4DF	28	21	28	47
Σ Cl_5DF	35	23	26	38
Σ Cl_6DF	36	14	30	41
Σ Cl_7DF	27	11	25	53
Cl_8DF	18	13	18	36
2,3,7,8-Cl_4DD	< 0.1	< 0.1	0.17	0.49
1,2,3,7,8-Cl_5DD	< 0.1	< 0.1	0.80	1.2
1,2,3,4,7,8-Cl_6DD	0.92	1.9	0.82	2.5
1,2,3,6,7,8-Cl_6DD	2.2	4.3	3.1	5.9
1,2,3,7,8,9-Cl_6DD	1.7	2.4	2.0	4.0
1,2,3,4,6,7,8-Cl_7DD	24	40	42	60
2,3,7,8-Cl_4DF	2.4	4.4	2.0	4.8
1,2,3,4/7,8-Cl_5DF	6.6	4.0	0.43	4.1
2,3,4,7,8-Cl_5DF	3.0	3.2	1.6	3.6
1,2,3,4,7,8/9-Cl_6DF	4.4	5.5	1.8	4.6
1,2,3,6,7,8-Cl_6DF	4.6	2.5	2.9	5.3
1,2,3,7,8,9-Cl_6DF	<0.5	<0.5	<0.5	<0.5
2,3,4,6,7,8-Cl_6DF	3.0	1.6	1.9	4.0
1,2,3,4,6,7,8-Cl_7DF	17	6.6	14	29
1,2,3,4,7,8,9-Cl_7DF	1.9	0.77	1.0	1.9
TEQ	**4.4**	**5.3**	**3.7**	**7.6**

The highest concentrations of the higher chlorinated PCDD/F were found in sewers which carried primarily household wastewater and occasionally runoff water but without any industrial influence. The homolog profile agreed well with those in household wastewater and sewage sludge [11]. In contrast, higher concentrations of the lower chlorinated PCDD/F were found in the sewers with no contributions from household wastewater. The profiles from these latter samples were similar to the atmospheric patterns found in the surface runoff, but distinctly different from the pattern observed in sewage sludge. This was one of several pieces of evidence suggesting that household wastewater was an important source of PCDD/F in sewage sludge.

The TEQ-concentrations found in sewer sediments were distinctly lower than those found in sewage sludge from the MWTP in Bayreuth. During a sampling period in 1991 TEQ-concentration between 16 pg/g and 60 pg/g were detected in more than 25 sludge samples.

Household Wastewater

Household wastewater samples were collected on two different days (a Tuesday and a Friday) at an apartment building in Bayreuth (FRG). The apartment building had approximately 750 inhabitants and no commercial space. The building drainage for roof runoff and household wastewater were led through separate piping systems which made it possible to collect samples containing only household wastewater. The samples were collected with a ladle as the water fell over a weir. This allowed a representative sampling of the wastewater including the solid material. One ladle was collected every 5 minutes. The water collected over one hour was pooled to give a 3-4 L sample. The results are given in Table 4 along with the water quantity used in the building during the sampling periods and the total amount of water used over the day.

Table 4: PCDD/F in household wastewater (pg/L)

Household Wastewater:	**Friday 15.11.91**	**Friday 15.11.91**	**Friday 15.11.91**	**Tuesday 31.03.92**	**Tuesday 31.03.92**	**Tuesday 31.03.92**	**Tuesday 31.03.92**	**Tuesday 31.03.92**
Sampling time	7:00-8:00	11:00-12:00	15:00-16:00	7:00-7:30	9:20-9:40	11:00-11:30	14:50-15:05	21:50-22:10
Water quantity per hour	5.75 m³	4.17 m³	3.99 m³	6.60 m³	5.04 m³	3.33 m³	2.97 m³	1.00 m³
Water quantity per day	80.3 m³			84.0 m³				
Σ Cl_4DD	2.4	11	6.6	1.4	4.9	6.0	1.9	1.2
Σ Cl_5DD	15	46	89	4.8	18	31	11	5.6
Σ Cl_6DD	11	110	130	6.3	23	36	12	8.8
Σ Cl_7DD	62	1100	920	15	97	170	28	24
Cl_8DD	360	4500	2600	100	690	840	170	100
Σ Cl_4DF	7.1	26	19	5.8	16	18	9.7	7.9
Σ Cl_5DF	4.5	20	11	3.2	11	13	6.7	3.2
Σ Cl_6DF	5.3	30	15	2.9	10	15	6.7	2.8
Σ Cl_7DF	5.5	49	25	3.9	17	27	9.3	5.0
Cl_8DF	6.0	40	24	3.5	12	23	7.6	6.0
2,3,7,8-Cl_4DD	< 0.1	< 0.1	< 0.1	< 0.1	< 0.3	< 0.3	< 0.3	< 0.2
1,2,3,7,8-Cl_5DD	< 0.1	0.38	0.22	0.29	0.15	0.24	0.32	0.10
1,2,3,4,7,8-Cl_6DD	< 0.1	0.80	0.20	0.30	< 0.1	< 0.1	< 0.1	< 0.1
1,2,3,6,7,8-Cl_6DD	1.1	9.4	14	2.1	3.2	1.7	1.7	1.0
1,2,3,7,8,9-Cl_6DD	0.56	3.1	3.6	0.72	1.3	0.68	0.95	0.45
1,2,3,4,6,7,8-Cl_7DD	31	550	600	8.7	53	94	17	13
2,3,7,8-Cl_4DF	0.39	1.4	0.83	1.4	1.9	1.6	3.3	0.92
1,2,3,4/7,8-Cl_5DF	< 0.1	0.63	0.54	<0.1	0.45	0.56	0.59	< 0.1
2,3,4,7,8-Cl_5DF	0.46	1.6	1.1	0.83	0.78	0.61	0.36	0.10
1,2,3,4,7,8/9-Cl_6DF	0.50	1.3	1.0	0.59	1.4	< 0.1	< 0.1	< 0.1
1,2,3,6,7,8-Cl_6DF	0.54	4.2	2.5	0.39	0.93	< 0.1	< 0.1	< 0.1
1,2,3,7,8,9-Cl_6DF	< 0.1	0.83	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
2,3,4,6,7,8-Cl_6DF	0.51	1.5	1.2	< 0.34	1.0	< 0.1	< 0.1	< 0.1
1,2,3,4,6,7,8-Cl_7DF	0.29	28	12	2.3	10	16	6.2	3.1
1,2,3,4,7,8,9-Cl_7DF	0.17	0.96	0.66	0.10	0.40	0.61	0.26	0.15
TEQ	**1.4**	**14**	**12**	**1.7**	**3.1**	**3.3**	**1.8**	**0.81**

The PCDD/F concentrations found in the household wastewater differed significantly in the course of one day and also between the two days. The highest concentrations were found during daytime. In the morning and also in the evening the PCDD/F-concentrations were much lower. The concentrations were up to 10 times higher than in the runoff samples.

An attempt at a crude mass balance with these data was made in another paper [10]. The flux of the PCDD/F in TEQs into the Bayreuth MWTP was estimated to be 8 times higher from household wastewater than from surface runoff. Also, the homolog profile differed between the two kinds of samples. The profile in household wastewater agreed well with the profile in sewage sludge whereas the profile in runoff samples was distinctly different (see above). The daily cycle in the household wastewater concentrations and observations of wastewater colour and consistency led us to suspect washing effluent as a possible PCDD/F source.

Washing Machine Effluent

Following up on the results of the last section, washing machine effluent samples were analysed for PCDD/F. Washing machine effluent was collected in different households and from different kinds of clothing. All wastewater from one washing cycle was collected in a big tub and mixed well. For each analysis 1-2 L of effluent were transferred to a glass jar and transported to the lab. A method blank was obtained by running the washing machine through its cycle with detergent but without clothes. The PCDD/F concentrations in the blank were at least a factor of 100 lower than those present in the samples with laundry. Hence, neither the detergent nor the machine itself nor the sampling procedure was the source of the PCDD/F.

The washing temperature varied depending on the type of laundry: white clothes were washed at 95°C, baby wash and dark coloured clothes at 60°C, and bright coloured clothes at 40°C. Table 5 gives the PCDD/F concentrations found in the different washing machine effluent samples. The PCDD/F flux per load of wash can be easily calculated by multiplying the volume of water by the concentration.

All four washing machine effluent samples had the same homolog profile that was found in household wastewater and sewage sludge [10,11]. The concentrations ranged up to 25 pg TEQ/L and varied by only a factor of 2 in the 4 samples. The homolog concentrations in the washing machine wastewater were very similar to those measured in the most contaminated household wastewater samples.

In further studies it was shown that textiles were contaminated with PCDD/F [11,12,19]. In order to examine the fate of PCDD/F on textiles during washing an experiment was conducted in which two mildly contaminated cotton T-shirts containing altogether 280 ng ΣPCDD/F (620 pg TEQ) were washed together with two uncontaminated cotton undershirts (1.5 ng ΣPCDD/F or 8 pg TEQ on both undershirts). After washing it was found that 16% of the PCDD/F (19% of the TEQ) originally present in the contaminated T-shirts was in the washing machine effluent and 7% (8% of the TEQ) in the previously uncontaminated undershirts [11]. Another experiment under somewhat different conditions (an analysed T-shirt with 3 kg common dirty wash) gave similar results: 35% of the PCDD/F were removed from the T-shirt during washing. This demonstrates that PCDD/F are not tightly bound to the fabric and washing out of these compounds does occur.

Tab. 5: PCDD/F-concentrations in washing machine effluent (pg/L)

Samples:	**Dark coloured cloth**	**White cloth**	**Bright colored cloth**	**Baby cloth**
Water quantity per wash: Textiles per wash:	82 l 4 kg	57 l 2 kg	67 l 3.2 kg	86 l 3 kg
Σ Cl_4DD	30	40	31	21
Σ Cl_5DD	110	80	130	60
Σ Cl_6DD	330	240	530	170
Σ Cl_7DD	1100	630	1600	990
Cl_8DD	4100	2300	3600	4400
Σ Cl_4DF	81	120	97	71
Σ Cl_5DF	67	150	120	100
Σ Cl_6DF	160	120	190	310
Σ Cl_7DF	500	180	470	510
Cl_8DF	380	160	300	430
2,3,7,8-Cl_4DD	< 1	1.6	1.0	< 0.5
1,2,3,7,8-Cl_5DD	1.9	1.7	1.9	1.7
1,2,3,4,7,8-Cl_6DD	3.5	< 0.5	3.2	< 0.5
1,2,3,6,7,8-Cl_6DD	22	13	24	23
1,2,3,7,8,9-Cl_6DD	5.9	6.9	9.2	6.8
1,2,3,4,6,7,8-Cl_7DD	540	270	600	570
2,3,7,8-Cl_4DF	7.4	8.3	5.9	4.3
1,2,3,4/7,8-Cl_5DF	2.1	5.7	3.1	3.3
2,3,4,7,8-Cl_5DF	4.2	4.9	4.6	9.8
1,2,3,4,7,8/9-Cl_6DF	4.9	4.2	4.2	8.5
1,2,3,6,7,8-Cl_6DF	6.5	6.1	7.9	7.5
1,2,3,7,8,9-Cl_6DF	< 0.5	< 0.5	< 0.5	< 0.5
2,3,4,6,7,8-Cl_6DF	12	8.2	9.7	5.8
1,2,3,4,6,7,8-Cl_7DF	330	120	300	200
1,2,3,4,7,8,9-Cl_7DF	3.8	4.5	2.1	8.8
TEQ	**25**	**17**	**24**	**25**

Shower Water

Shower and bath water represent another potential source of PCDD/F to household wastewater. In average of Germany 30% (= 43 L) of the total daily water consumption is used for this purpose [20]. It was demonstrated that PCDD/F can transfer from contaminated textiles to the skin's surface [11], and it was thought that these PCDD/F on the skin's surface might be removed during washing and contribute to the PCDD/F levels in household wastewater. In order to test this hypothesis the shower water from 5 individuals was analysed. As the concentrations depend on the water quantity used for each shower, the results in Table 6 are given in pg/shower and not pg/L.

The PCDD/F-quantities in the shower water differed by nearly two orders of magnitude. This variability can be explained by the variability in textile contamination and hence in the expected skin contamination. The PCDD/F-homolog profile agreed well with typical profiles in textiles [12,19] and was similar to the profile found in household wastewater (→ Table 3) and in sewage sludge. These results show that wash water contributes to the PCDD/F load in household wastewater and are consistent with the hypothesis that skin is the source.

Tab. 6: PCDD/F-quantities in shower water (pg)

Shower water: (water quantity)	**Sample 1** (13 litres)	**Sample 2** (25 litres)	**Sample 3** (19 litres)	**Sample 4** (7.5 litres)	**Sample 5** (5 litres)
Σ Cl_4DD	62	80	70	26	60
Σ Cl_5DD	83	200	150	71	84
Σ Cl_6DD	640	1700	510	290	280
Σ Cl_7DD	8500	5000	1500	980	60
Cl_8DD	120000	15000	7600	4000	1900
Σ Cl_4DF	1200	150	300	170	200
Σ Cl_5DF	1100	300	290	200	160
Σ Cl_6DF	1600	880	400	150	110
Σ Cl_7DF	2100	1400	440	120	72
Cl_8DF	2500	1300	230	90	60
2,3,7,8-Cl_4DD	4.7	< 10	< 5	< 2	< 2
1,2,3,7,8-Cl_5DD	< 2	< 10	< 5	< 2	< 2
1,2,3,4,7,8-Cl_6DD	< 2	< 10	< 5	< 2	< 2
1,2,3,6,7,8-Cl_6DD	68	130	40	19	< 2
1,2,3,7,8,9-Cl_6DD	26	58	< 5	< 2	< 2
1,2,3,4,6,7,8-Cl_7DD	4800	2400	670	440	240
2,3,7,8-Cl_4DF	9.6	< 10	13	11	9.0
1,2,3,4/7,8-Cl_5DF	< 2	< 10	< 5	< 2	< 2
2,3,4,7,8-Cl_5DF	21	28	19	14	10
1,2,3,4,7,8/9-Cl_6DF	< 2	50	< 5	11	13
1,2,3,6,7,8-Cl_6DF	< 2	65	< 5	5.9	< 2
1,2,3,7,8,9-Cl_6DF	< 2	< 10	< 5	< 2	< 2
2,3,4,6,7,8-Cl_6DF	<35	53	<20	9.0	< 2
1,2,3,4,6,7,8-Cl_7DF	1400	730	230	74	48
1,2,3,4,7,8,9-Cl_7DF	21	25	< 5	< 2	< 2
TEQ	**210**	97	**34**	**21**	**12**

Acknowledgements

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From: erg!ERG-MA!JCANTIN@uunet.uu.net (Jeff Cantin)
Date: 04-Oct-95 15:59:00 -0300
To: BSMITH@TX.NCSU.EDU (Brent Smith2)
Subject: Coming soon to your mailbox...

The document is completed and was sent to Doug Williams at EPA this week. sent our original out to have a couple of copies made and will send one to you as soon as it returns. It wouldn't hurt to go over it and take note o anything that looks funny or merits change after a fresh look at it. Bett to make any changes now before it goes to printing. I suspect Doug will show it to a short list of people at EPA and then submit it for printing shortly.

I am working with Bob Pojasek on another project and he told me he was dow at ATMI last week giving a presentation on P2. Something like 85 people showed up which he thought was encouraging. He said Jane Henricks told hi they were very happy that EPA had taken it upon themselves to do a documen for the industry and that they thought it would serve a real need.

Bob also mentioned there was some talk about a recent study where they sampled household laundry wastewater and found PCDDs and PCDFs. It seemed implicate textile finishing chemicals (bleaches? dyes?) as dioxin precursors, adn they specifically mentioned denim. Even wierder was that they found trace quantities in greywater from showers, as if the chemicals had been transferred to the body and then rinsed off during showering. Of course we are talking ppq here. The reference is Chemosphere vol 31, No. p. 2887-2896 and the author is Horstmann (cited in our document also?).

Heard anything about it?
Any ideas on the PCDD/F formation mechanism?
Any P2 options for reducing potential for formation?
Any chance this will become a big issue for the industry, in the same way dioxin in pulp effluent did for pulp and paper?

See reply