Dioxin '97, Indianapolis, Indiana, USA

Decrease in the Concentrations of PCDDs and PCDFs in Sewage Sludge from Switzerland

C. Rappe[1], R. Andersson[1], C. Studer[2], G. Karlaganis[2]

1) Institute of Environmental Chemistry, Umeå University, S-901 87 Umeå, Sweden
2) Federal Office of Environment, Forests and Landscape, CH-3003 Bern, Switzerland

ABSTRACT

In the present study the PCDD and PCDF contamination of sewage sludge samples from 1989/90 is compared with the new samples collected in 1995 from the same locations. The samples were analysed by HRGC/GRMS. In eight out of ten samples the PCDDs and PCDFs concentrations show a more or less pronounced decrease. For two locations no such trend could be observed. Possible sources are discussed.

Key words: Sewage sludge, PCDD, PCDFs, Polychlorinated dioxins, Polychlorinated dibenzofurans, Switzerland, Time trend, Decrease

INTRODUCTION

The contamination of PCDDs and PCDFs in sewage sludge is well documented. Analytical results have been reported from United States, Germany, Sweden, Canada and United Kingdom. At DIOXIN '94 in Kyoto we presented a study including 30 samples of sewage sludge from Switzerland (1). It is also well established that the concentrations of PCDDs and PCDFs in our environment are decreasing, including the human body burden as indicated by analyses of human milk. In a recent study WHO found that the annual decrease of TEQ in human milk was 5-15% (2). Very few studies have been performed to prove a downgoing trend of PCDDs and PCDFs in sewage sludge. Due to the large variation between individual municipalities (1,3), such a study should be performed by analyzing samples from the same treatment plant (POTW) at known intervals. In the present study we have resampled in 1995 the sludge from ten of the POTWs included in the 1989/90 study (1).

EXPERIMENTAL

Sampling sites

Site one and two are small villages located at an altitude between 1100 and 1250 m.

The areas contain no known sources of chlorinated pollutants. Site three and four are middle sized towns. They have MSW incinerators, but no other identified source of PCDDs and PCDFs. Site five is a small town with only small industries of a type not recognized as a source of PCDDs and PCDFs. Site six received only and site seven mostly effluents from the chemical industries. Site eight receives only effluents from a mill producing bleached pulp. Site nine and ten are villages with textile industries.

The size and technology of the investigated treatment plants are summarised in Table 1.

Table 1. Information on the selected sewage treatment plants

Site	Origin	Size (1993)			Technology (1993)	
		IE*	Influent (m3/d)		Prelimination	Sewage sludge treatment
			Domestic	Industry		
1	UNP	183	37	0	no	anaerobic mesophilic digestion/storage → agriculture
2	UNP	160	no information		no	anaerobic mesophilic digestion/storage → agriculture
3***	BIGIN	187'500	76'500		yes	anaerobic mesophilic digestion → dewatering → incineration/ landfill
4	BIGIN	216'667	37'000	3'000	yes	dewatering → incineration
5	SMAIN	104'933	22'464	1'296	yes	dewatering → landfill
6	CHEM	726'667	0	35'000	no	dewatering → incineration
7	CHEM	423'433	1'122	17'023	yes**	thickening → dewatering → incineration
8	PAP	291'250	0	no inf.	no	incineration
9	TEX	43'133	8'165	4'165	yes	anaerobic mesophilic digestion → agriculture
10***	TEX	27'500		11'000	no	anaerobic mesophilic digestion → agriculture

UNP: plants from unpolluted areas. BIGIN: plants from large agglomerations with incinerator. SMAIN: plants from small agglomerations with incinerator. CHEM: plants from chemical industry. PAP: plants from paper industry. TEX: plants from textile industry.
* IE: inhabitant equivalents (60 g BODs/inhabitant-d). ** Because of suspended solids.
*** Includes domestic and industrial waste water.

Sampling procedure

Wet samples of 3 L of digested sludge were collected during the first half of 1989/90 and 1995 respectively and stored at 4°C before homogenization, frozen at -20°C and shipped for analysis. The origin of the samples was unknown for the analytical laboratory.

Analytical

All samples were dried in a gentle stream of air in the hood. Extraction of the sludge samples, clean-up of the extracts and the HRGC/HRMS analyses followed earlier described methods for sewage sludge and sediments (4,5).

RESULTS

In Table 2 we have collected the results of the analyses of the 1989/90 and the 1995 sampling campaigns. The results include the most toxic 2,3,7,8-substituted congeners and the sum of all isomers in a congener group. We also give the TEQ values according to the WHO model (6) and the D/F Ratio which is the ratio Σ PCDDs/Σ PCDFs.

DISCUSSION

In the two remote villages (site one and two) the concentration of PCDDs, PCDFs and TEQ were low already in the 1989/90 sampling. The concentrations have now decreased by 35-50%. These two villages are representative of the situation in pristine areas. In site three we have observed a decrease by a factor of 13, but there is, to our knowledge, no obvious reason for this decrease.

In site four the situation is quite different, the TEQ-value for the 1995 samples is in fact higher than for the two samples collected in 1989/90. We have observed that the dominating congeners in all three samples are 2,3,7,8-tetraCDD and 1,2,3,7,8-pentaCDD, both for the TEQ-values and within the group of isomers as well. This is quite unusual. These two congeners are associated with the production and purification (distillation residues) of 2,4,5-trichlorophenol (7). However, no such production is known to have taken place in this region of Switzerland.

The most dramatic decrease (more than hundred times) was found in site five. In the 1989/90 sample we found a pronounced dominance by the tetra-, penta-, hexa- and hepta-CDFs. Since this community has no specific industries, the most plausible source of this contamination could be a fire or an accident in electrical equipment containing PCB (transformers, capacitors) in connection with the 1989/90 sampling. In 1995 the pattern of the sample from this community is not dominated by PCDFs.

The dramatic reduction of PCDDs, PCDFs and TEQ in the sewage sludge from the

chemical industries (site six) is probably due to changes in the production at these factories. Another factor could be the increased awareness of environmental problems caused by the production and use of chlorinated compounds and solvents. The chemical factory connected to site seven is obviously operating on a campaign basis. We have two relatively high readings here and one very low. In addition the fingerprint in the 1995 sample is dominated by PCDFs while in the 1989/90 high sample the PCDDs were found to dominate.

We observed the reduction of TEQ for site eight to be by a factor of nine. This is due to the change in bleaching technology in the pulp mill and the campaign-wise production in the different production lines with different bleaching technologies. In the earlier sample we also observed a series of alkylated PCDFs, which are known indicators of pulp bleaching using free chlorine (8). In 1989/90, site nine and ten had high concentrations of octa- and heptaCDD, a clear indication that pentachlorophenol treated cotton or chloranil derived dyes were used in the local textile industries. Now we find that the concentrations have decreased by a factor of seven or eight.

CONCLUSIONS

In the samples from sewage treatment plants that we collected and analyzed both in 1989/90 and now in 1995 we have found a downgoing trend in PCDDs, PCDFs and TEQ in eight out of ten samples. The decrease was more pronounced in the samples that were high in 1989/90 than in those which were low already at that time. This is the first study showing such a trend where samples from the same plants have been analyzed and compared.

For two of the samples (site four and seven) no such decrease could be observed. The sample from site seven is closely related to chemical production, but for site four no such correlation could be found, although this sample has a fingerprint typical to the production or purification of 2,4,5-trichlorophenol (7).

REFERENCES

1. Rappe C., Andersson R., Karlaganis G. and Bonjour R., Organohal. Comp., **20**, 79-84 (1994).
2. WHO. Environmental Health in Europe, **3** (1996).
3. US EPA National Sewage Sludge Survey, PB 90-107491 (1989).
4. Rappe, C., Kjeller, L.-O. and Andersson, R., Chemosphere, **19**, 13-20 (1989).
5. Kjeller, L.-O., Kulp, S.E., Jonsson, B. and Rappe, C., Toxicol. Environ. Chem. **39**, 1-12 (1993).
6. Ahlborg, U.G. Organohal. Compd., **21**, 11-13 (1994).
7. Littorin, M., Hansson, M., Rappe, C., Kogevinas, M. Lancet, **344**, 611-612 (1994).
8. Buser, H.-R., Kjeller, L.-O., Swanson, S.E., Rappe, C. Environ. Sci. Technol. **23**, 1130-1137.

Table 2. Concentrations of PCDDs and PCDFs in 1989/90 and 1995 sewage sludge samples from Switzerland. (pg/g d.w.)

	Site 1		Site 2		Site 3		Site 4			Site 5	
	89	95	89	95	89	95	89	90	95	89	95
2378-TCDF	5.1	2.7	10	2.7	22	4	160	160	290	470	5.5
SUM TCDF	42	6	47	9.2	130	6.4	1900	3800	1100	2900	11
2378-TCDD	ND(1.5)	ND(0.12)	1.7	0.65	1.2	0.31	34	54	77	75	0.34
SUM TCDD	ND(22)	0.16	15	28	88	0.31	540	1500	180	300	0.91
23478-PeCDF	2.8	3	3.5	0.52	21	5.2	520	680	870	1100	8.1
SUM PeCDF	52	29	41	33	220	7.5	6200	7600	4900	16000	89
12378-PeCDD	3	1	1.8	1.3	4	1.2	230	480	670	330	1.8
SUM PeCDD	35	8.1	43	6.4	510	3.8	3200	5100	2800	3000	24
SUM HxCDF	36	68	43	51	470	23	14000	14000	14000	19000	110
SUM HxCDD	130	100	100	65	2300	61	5800	11000	9400	6500	73
SUM HpCDF	140	200	91	100	680	63	4100	17000	11000	23000	130
SUM HpCDD	500	360	1300	300	4800	200	15000	19000	9400	14000	190
OCDF	ND(38)	340	100	100	830	41	8200	8500	3600	ND(42)	60
OCDD	4300	1400	5700	1800	22000	870	26000	27000	5400	19000	650
I-TEQ	15	9.7	21	8.4	130	10	1200	1700	2200	1900	16
D/F Ratio	18.4	2.91	22.2	7.5	12.7	8.06	1.47	1.25	0.786	0.703	2.34

	Site 6			Site 7			Site 8		Site 9		Site 10	
	89	90	95	89	90	95	89	95	89	95	89	95
2378-TCDF	79	45	9.1	92	1.3	110	60	10	100	16	ND(13)	28
SUM TCDF	2600	740	52	860	23	320	140	24	400	25	ND(360)	62
2378-TCDD	23	6.2	0.86	25	2.2	5.8	0.91	0.92	1.3	0.27	ND(4.2)	0.75
SUM TCDD	1800	510	2.9	460	11	13	36	4.3	42	2	ND(64)	3.2
23478-PeCDF	350	120	9.1	69	1.8	61	1.4	0.94	48	8.3	ND(8.8)	7.6
SUM PeCDF	5300	1700	71	490	29	310	10	15	390	13	ND(170)	28
12378-PeCDD	260	80	3.7	86	ND(1.8)	19	1.9	0.57	13	ND(1.4)	ND(6.5)	2.6
SUM PeCDD	7900	2900	42	1300	12	77	10	6.4	200	1.7	ND(84)	24
SUM HxCDF	9700	2200	120	330	ND(27)	430	14	18	700	38	ND(200)	27
SUM HxCDD	20000	6900	130	7800	ND(29)	240	23	14	900	59	430	70
SUM HpCDF	13000	3100	240	240	ND(33)	1600	42	83	720	120	ND(26)	380
SUM HpCDD	46000	14000	290	4200	60	270	210	170	4800	280	13000	500
OCDF	13000	6500	390	1400	ND(33)	800	35	120	570	160	ND(150)	320
OCDD	67000	20000	890	19000	360	410	3800	1500	24000	1400	51000	2200
I-TEQ	1400	390	22	230	6.2	120	14	6.1	120	15	150	23
D/F Ratio	3.27	3.11	1.55	9.87	8.52	0.292	16.9	6.52	10.8	4.9		3.42