PCDDs and PCDFs in Samples of Sewage Sludge from Various Areas in Switzerland

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Abstract

We have analyzed 30 samples of sewage sludge from Switzerland. The samples were collected in urban as well as in very rural areas. All samples were found to be contaminated by both PCDDs and PCDFs, also the samples from the most rural areas. The concentrations ranged from 6 pg TEQ/g dry matter (d m) to 4100 pg TEQ/g d m. In general the concentrations were found to be higher in the urban areas, the highest concentrations could be correlated to local industrial point sources. In all cases the congener pattern was dominated by octa- and hepta CDDs, the concentrations of the toxic 2,3,7,8-substituted congeners are normally quite low, in a few cases even below the detection limit (1 pg/g d m). Some tetra- and penta chlorinated congeners can serve as markers for a typical sewage sludge pattern. Washing of pentachlorophenol treated textiles and biological dioxin formation within the sewer system are suggested to give the major contribution to the identified background concentrations.

Introduction

In 1983, Lamparski et al. reported on the occurrence of PCDDs and PCDFs in samples of sewage sludge from USA, including an archived sample from 1933 from Milwaukee. In all samples they found low concentrations of tetra-, penta- and hexa-chlorinated PCDDs and PCDFs, below 15 pg/g d m, much higher values were reported for hepta- and especially for octa-CDD, up to 10 000 pg/g d m (1).

In 1985 Weerasinghe et al. reported on two samples of sewage sludge from the state of New York. The concentrations found in a sample from an urban area were in general 5-10 times higher than the concentrations found in the sample from the rural area. The sample from the urban area was reported to contain 60 000 pg octa CDD/g d m (2).

Hagenmaier et al. (3) performed a survey in 1986 of the contamination of PCDDs and PCDFs in 43 samples as sewage sludge collected in various parts of Germany. They reported on values as high as 75 000 pg hepta CDD/g d m and 200 000 pg octa CDD/g d m (3).

All these early studies discussed above and also most of the subsequent studies published in the 90s were reported by the congener group (profiles) and by the toxic congeners, but the detailed picture of the individual toxic and nontoxic congeners (patterns) has not been discussed.

In 1989 Rappe et al (4) reported on two samples of sewage sludge from Sweden. One of the samples was from Stockholm and the other from a rural area where the sewer system only received water from households. The concentrations of congener profiles and congener patterns were quite similar in the two samples in spite of their large difference in origin. A series of individual tetra-, penta-, hexa- and heptachlorinated PCDD and PCDF congeners were identified in addition to the toxic 2,3,7,8-substituted congeners (4).

In the present study we report on the analysis of 30 samples of sewage sludge collected in urban and rural areas in Switzerland. In the analytical work we have used methods, which allow congener specific identification of individual PCDD and PCDF congeners as described earlier (4-6).

Materials and Methods

The samples were collected in the storage basin of the municipal sewage systems at two different occasions: during March-April 1989 and June 1990 from 30 different communities in Switzerland representing eight different categories of population density and industrial activity. Three samples were unclassified.

A. Totally uncontaminated areas, 100-150 persons
B. Low contaminated areas
C. Large cities with MSW incineration, the population exceeding 100 000 person equivalents
D. Small cities with MSW incineration
E. Large cities without MSW incinration
F. Areas with chemical industries
G. Areas with pulp and paper industries
H. Areas with textile industry
U. Unclassified.

For the extraction, clean-up of the extract and the HRGC/HRMS analyses as well as the isomer identification we followed earlier described methods (4-6). For the calculation of the toxic equivalents (TEQ) we used the I-TEF/89 system (7).

Results

A. Concentrations

The concentrations of octa CDD and TEQ for the 30 samples analyzed in the present study are collected in Table 1. Counted as TEQ, the difference between the highest and the lowest value is more than a factor of 500. For comparison it can be noted that the two samples from Sweden earlier analyzed contained both 23 pg TEQ/g d m (4). In the totally 30 samples analyzed in this study we found the following distribution

1. < 50 pg TEQ/g d m	13 samples
2. 50 - 100 pg TEQ/g d m	7 samples
3. 100-300 pg TEW/g d m	5 samples
4. < 300 pg TEQ/g d m	5 samples

1. Concentrations below 50 pg TEQ/g d m were found for all 5 samples from the totally uncontaminated area but also in 8 other samples representing large cities with or without MSW incineration as well as from areas with chemical industry and pulp and paper industry.
2. Concentration in the range 50-100 pg TEQ/g d m was found in 3 out of 4 small cities with MSW incineration and also in one sample in each of the following categories: C, F, G and H.
3. Of the 5 samples with a concentration in the range of 100-300 pg TEQ/g d m two samples came from areas with textile industry. One of these samples was very high in hepta- and octa CDD, these two congeners make up most of the TEQ found in this sample. This is a clear indication of a point source using pentachlorophenol. The other samples in this group represent category C and F (two samples).
4. Concentrations exceeding 300 pg TEQ/g d m were found in two unclassified samples and one each from category C, D and F.

B. Profiles

In all samples below 50 pg TEQ/g d m the congener profile (the ratio between the sum of all congeners with the same chlorination level) are totally dominated by the hepta- and octa CDD at concentrations as high as 67 000 pg octa CDD/ g d m. The samples

containing higher values of TEQ than 100 pg/g have normally concentrations of octa CDD, above 10 000 pg/g, but in several of the samples with the highest concentrations of TEQ, the lower chlorinated congener groups gave the main contribution.

C. Patterns

Samples influenced by point sources have patterns influenced by these point sources as well. All samples having concentrations below 50 pg TEQ/g d m, which can be considered to be background concentrations have very similar pattern for tetra-, penta- and hexachlorinated PCDDs and PCDFs. This could be considered as a typical "sewage sludge pattern". It is interesting to point out that the same specific sludge pattern can be found in samples from totally uncontaminated areas as well as in sludge samples from large cities with or without MSW incineration, in areas with chemical as well as pulp and paper industries. These patterns for the Swiss samples for tetra-, penta- and hexachlorinated PCDDs and PCDFs are essentially the same as the patterns earlier reported from the rural area in Sweden, receiving water from households only (4). The major congeners in the typical sewage sludge patterns are listed in Table 2.

Discussion

The results reported on here in this study show that PCDDs and PCDFs found in sewage sludge samples from Switzerland differ in concentrations by a factor of 500 but also in profiles and patterns. Sewage sludge is a useful matrix for the identification of local or regional contamination sources. In general the concentrations in these Swiss samples are lower than those earlier reported from Germany (3).

Of special interest is to discuss the background samples because the patterns found in these low contaminated samples are independent if these samples originate from rural or urban areas in Switzerland and Sweden. A number of possible sources can be discussed in connection with these background samples.

1. Local sources like MSW incinerators and traffic. Such sources seem to be excluded due to the fact that this typical sewage sludge pattern was also found in samples from areas without MSW incineration and traffic. In addition, car emissions have much higher concentrations for the lower chlorinated congeners as compared to the hepta- and octa CDD (8, 9).
2. Long range transport followed by dry and wet deposition. It has been reported by Tysklind et al (10) that there is a difference in profiles in air samples. In samples collected far from the source the octa CDD was the major congener group, but this was not the case in samples collected close to the source. However, both local and

long range transport is not in agreement with the observation of the same typical pattern in a Swedish sewer system only receiving household water (4).

3. Washing of textiles treated with pentachlorophenol. Horstmann et al. have recently reported on the similarity between the PCDD pattern found in sewage sludge and in water from washing of textiles treated with pentachlorophenol (11). In both cases the congener profiles were dominated by the higher chlorinated dioxins.
4. Biological formation within the sewer system. Using ^{13}C-labelled pentachlorophenol Öberg et al. (12) have found that incubation of sewage sludge treated with this compound could generate ^{13}C-labelled octa CDD. Since ^{13}C-labelled compounds are not found in the environment, this experiment has proven the biological formation of higher chlorinated dioxins within the sewer system. As pointed out by Horstmann (11) treatment of textiles with pentachlorophenol is still very frequent, especially cotton products imported from the third world.

Conclusions

The PCDDs and PCDFs found in background samples of sewage sludge are best explained by direct contamination by pentachlorophenol and by secondary biological reactions in the sewer system.

Table 1. Concentrations of OCDD and TEQ (pg/g d m) found in the samples analyzed

Category	OCDD	TEQ	Category	OCDD	TEQ
A	5700	21	E	11000	35
A	4300	15	F	67000	4100
A	5000	25	F	19000	230
B	1400	9	F	3300	190
B	17000	46	F	15000	55
C	24000	71	F	4300	11
C	22000	130	F	630	8
C	26000	1100	G	3800	14
C	4900	17	G	8500	53
C	9800	43	H	24000	120
D	14000	57	H	20000	57
D	5400	79	H	51000	150
D	5700	53	U	360	6
D	19000	1900	U	20000	390
E	8600	30	U	27000	1700

Table 2. Congeners found in sewage sludge

TetraCDFs:	1,3,4,6-/1,2,4,8-; 1,2,7,8-, 2,3,6,8-, 2,3,7,8- and 3,4,6,7-tetraCDF.
TetraCDDs:	1,3,6,8-, 1,3,7,9- and 1,4,6,9-/1,2,7,9- and very minor amount of 2,3,7,8-tetra CDD.
PentaCDFs:	1,2,4,6,8-, 1,2,3,6,8-/1,3,4,7,8-, 1,2,3,7,8-/1,2,3,4,8-, 2,3,4,8,9-/1,2,4,6,9-, 2,3,4,6,8-, 2,3,4,7,8- and 2,3,4,6,7-pentaCDF.
PentaCDDs:	1,2,4,6,8-/1,2,4,7,9-, 1,2,3,6,8-, 1,2,4,7,8- and 1,2,3,6,9 and very small amount of 1,2,3,7,8-pentaCDD.
HexaCDFs:	1,2,3,4,6,8-, 1,3,4,6,7,8-, 1,2,3,4,7,8-, 1,2,3,6,7,8-, 1,2,4,6,8,9-, 1,2,3,7,8- and 2,3,4,6,7,8-hexaCDF.
HexaCDDs:	1,2,3,4,6,7,8-/1,2,4,6,7,9-/1,2,4,6,8,9-, 1,2,3,6,7,9-/1,2,3,6,8,9-, 1,2,3,4,7,8- and 1,2,3,6,7,8-hexaCDD.

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