Decline in PCDD and PCDF Levels in Sewage Sludges from Catalonia, Spain.

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Introduction

Sewage sludge samples from 10 different rural and urban waste water treatment plants (WWTPs) in Catalonia (Spain) were analysed for PCDDs and PCDFs. Total I-TEQ values for these samples ranged from 13 to 158 pg/g. Archived sewage sludge samples collected and stored from 14 WWTPs between 1979 and 1987 were also analysed to gain some insight into temporal trends and possible variations in source inputs. Total I-TEQ values for archived samples ranged from 29 to 8288 pg/g, showing evidence that contemporary sewage sludge PCDD and PCDF concentrations have declined since the eighties. These changes in concentrations could reflect variations in PCDD and PCDF sources to the environment over time.

The fate of PCDDs and PCDFs in sewage sludges after agricultural application and discharge into the sea was also studied. The concentrations of PCDDs and PCDFs in soils were determined before and after the application of sewage sludges and a general increase was observed with the applied rate. The PCDD and PCDF levels from different sediment samples were determined and compared with a sediment sample from a sewage sludge dumping site, which showed the highest I-TEQ value.

Materials and Methods

The samples were manually ground before extraction. Ten g (d.w.) sludge samples and 25 g (d.w.) soil and sediment samples were spiked with a mixture of fifteen $^{13}C_{12}$-labeled 2378-substituted isomers (Wellington, Guelph, Canada) and extracted in a Soxhlet apparatus for 48 hours with toluene. After extraction, crude extracts were transferred to hexane and treated with H_2SO_4 conc., followed by purification via a 3-stage open column chromatographic procedure [1]. Samples were finally concentrated to incipient dryness prior to the addition of a mixture of $^{13}C_{12}$-1234-TCDD and $^{13}C_{12}$-123789-HxCDD as the recovery standard.

Purified PCDD / PCDF extracts were analysed by HRGC-HRMS on a Thermo 8060 gas chromatograph fitted with a DB-5 (J&W Scientific, CA, USA) fused-silica capillary column

(60 m x 0.25 mm ID, 0.25 μm film thickness) coupled to an AutoSpec-Ultima (Micromass, Manchester, UK) mass spectrometer operating in the electron impact ionization (electron energy 38 eV) at 10.000 resolving power. Quantitative determination was performed by the isotope dilution method using relative response factors (RRFs) previously obtained from five standard solutions (Wellington, Guelph, Canada).

Results and Discussion

The PCDD and PCDF I-TEQ values in the contemporary samples analysed are given in table 1, with levels lower than 100 pg I-TEQ/g (d.w.) for 73% of the samples studied. The results for the arhived samples are shown in table 2, and 58% of these samples exceeded the limit set for German norms.

The concentrations of the sum of PCDDs were higher than those of the sum of PCDFs, with the ratio $R_{(\text{I-TEQ PCDD}/\text{I-TEQ PCDF}s)}>1$ (except for Manresa XI-94, St. Fruitós XII-96 and Vilafranca III-97), with values ranged from 1 to 25 for the contemporary samples and from 4 to 120 for the archived samples. Lower chlorinated PCDDs are found in much lower concentrations than higher chlorinated PCDDs. The PCDD and PCDF distribution observed contrasts with the congener distribution found in stack gas emissions of waste incineration plants.

Table 1 I-TEQ Values (expressed in pg/g d.w.) in contemporary sewage sludge samples.

	Total PCDDs	*Total PCDFs*	*TOTAL I-TEQ*
Balaguer (V-95)	19.93	2.97	22.90
Figueres (XI-97)	11.50	11.04	22.54
La Bisbal (XI-94)	21.93	2.56	24.49
Manresa (XI-94)	18.82	23.60	42.42
Manresa (I-96)	29.27	28.98	58.25
Manresa (VII-96)	56.56	13.10	69.66
Manresa (X-96)	135.78	13.64	149.42
Manresa (XII-96)	71.78	14.23	86.01
Roses (XI-97)	9.61	3.47	13.07
St. Fruitós (XII-96)	11.74	39.04	50.78
Solsona (96)	112.06	14.35	126.41
Solsona (V-97)	16.88	1.46	18.34
Tossa (XI-97)	151.93	5.99	157.91
Vic (I-94)	11.76	2.72	14.48
Vilafranca (III-97)	39.54	68.50	108.04
Mean	47.94	16.38	64.31
Median	21.93	13.10	50.78

Table 2 I-TEQ Values (expressed in pg/g d.w.) in archived sewage sludge samples.

	Total PCDDs	*Total PCDFs*	*TOTAL I-TEQ*
Besós (1979)	165.15	7.23	172.39
Bogatell (1979)	108.93	15.96	124.87
Blanes (1979)	24.97	3.60	28.56
Castelldefels (1987)	102.27	6.58	108.84
Figueres (1979)	677.10	88.69	765.79
Figueres (1984)	218.99	39.53	258.52
Figueres (1984)	88.48	19.40	107.88
Figueres (1985)	125.71	25.06	150.77
Figueres (1986)	238.11	14.46	252.57
Figueres (1987)	109.01	17.81	126.82
Girona (1987)	39.53	6.18	45.68
Igualada (1987)	8219.06	68.53	8287.58
Manresa (1987)	2617.76	108.46	2726.22
Olot (1979)	974.88	52.92	1027.79
Portbou (1979)	51.89	5.25	57.12
Reus (1979)	70.45	7.00	77.45
Reus (1987)	68.79	14.91	83.71
Roses (1979)	52.56	19.03	71.59
Roses (1982)	98.28	8.53	106.81
Roses (1983)	45.77	10.33	56.10
St. Feliu (1987)	67.06	9.16	76.22
Tossa (1983)	64.38	9.47	73.85
Tossa (1987)	117.61	7.37	124.98
Vilafranca (1987)	50.61	4.85	55.46
Mean	599.89	23.76	623.65
Median	100.28	12.40	108.37

The study of the effects of PCDDs and PCDFs in sewage sludges applied to the soil was based on two experiments devised during the eighties [2]. The I-TEQ values of sludge treated areas were 1.2 to 2.8 times higher than the respective values of the non contaminated areas for the basic experiment, and from 7.4 to 11.6 times higher for the acid experiment. The latter values were consistent with the data obtained by Albrecht *et al.* [3], who found a factor increase of 10.

The study of the effects of PCDDs and PCDFs in sewage sludges discharged into the sea was based on the analysis of different sediment samples. The results are given in table 3, and the highest contamination was observed in the Besós sediment, which corresponded to a sewage sludge dumping site. It is also interesting to note that the ratio $R_{\text{I-TEQ PCDDs / I-TEQ PCDFs}}$ was <1 for all the sediments studied with the exception of the Besós sediment.

Table 3 I-TEQ Values (expressed in pg/g d.w.) in sediment samples.

	Total PCDDs	*Total PCDFs*	*TOTAL I-TEQ*
Llobregat river(*)	0.43	1.38	1.81
	1.25	1.63	2.88
	1.08	2.25	3.33
	3.53	3.10	6.63
Ebro river(*)	0.51	1.61	2.12
	0.10	0.32	0.42
	0.92	2.77	3.69
Venice lagoon[4]	0.54	4.80	5.34
	0.26	2.11	2.37
	0.75	3.07	3.82
	2.90	31.95	34.85
	0.39	1.92	2.31
Orbetello lagoon(*)	0.11	0.29	0.40
	0.99	6.09	7.08
	1.42.	2.69	4.11
	0.04	0.17	0.21
	0.09	0.25	0.34
Besós river	32.44	24.60	57.04

(*) *Data unpublished*

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