Decline in PCDD and PCDF Levels in Sewage Sludges from Catalonia (Spain)

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Nineteen sewage sludges from rural and urban wastewater treatment plants (WWTPs) in Catalonia (Spain) were analyzed for PCDDs and PCDFs using HRGC−HRMS to determine the present levels of contamination. Total I-TEQ values for these samples ranged from 7 to 160 pg/g, with a mean value of 55 pg/g and a median value of 42 pg/g. Moreover, archived sewage sludge samples collected and stored between 1979 and 1987 from 15 WWTPs were analyzed to gain some insight into temporal trends and possible variations in source inputs. Total I-TEQ values for archived samples ranged from 29 to 8300 pg/g, with a mean value of 620 pg/g and a median value of 110 pg/g. Our findings show that contemporary sewage sludge PCDD/F concentrations have declined since the 1980s. In addition to the variations in PCDD and PCDF concentrations, there were also some changes in the isomeric patterns. These variations in levels and isomeric patterns could reflect changes in PCDD and PCDF sources to the environment over time.

Introduction

A number of directives concerning wastewater sewage sludges have been issued in the past decade. For instance, the promulgation of the Directive COM 91/271 on wastewater treatment requires the installation of treatment systems in all towns with over 2000 inhabitants before 2005 (*1*). Estimates for the year 2000 predict an increase in sewage sludge production of 185% in Spain, which means about 250 000 ton per year in Catalonia.

The contamination of PCDDs and PCDFs in sewage sludge is well documented. Analytical results have been reported in the United States (*2*), Germany (*3, 4*), Sweden (*5*), the United Kingdom (*6*), and Switzerland (*7*). However, there are no data as far as Spain is concerned. It is well-known that concentrations of PCDDs and PCDFs in the environment are decreasing. Declines in PCDD and PCDF fluxes to the environment and concentrations in biota have been reported in several studies in industrialized countries. In particular, there are data on air concentrations in Germany (*8*) and the United Kingdom (*9*), sediment cores from various countries (*10*−*12*), bird's eggs from the Baltic Sea (*13*), German cow's milk (*14*), and human tissue from a number of countries (*15*−*17*). However, very few studies have been performed to confirm a downward trend of PCDDs and PCDFs in sewage sludge. There is limited information about PCDD/F levels in archived sewage sludges in the literature. Lamparski et al. (*18*) reported PCDD/F levels in one 1933 archived sludge sample and compared these to contemporary levels from the same WWTPs. Jones et al. (*6, 19*) pointed to a fall in PCDD and PCDF concentrations in sewage sludge from Germany and the United Kingdom in recent years. Sewage sludge samples from Switzerland and Sweden have also shown a decrease during the period from 1989 to the present (*20*).

The aim of this study was to determine the PCDD and PCDF levels in sewage sludges from Spain and compare them with the levels from samples taken between 1979 and 1987 in order to detect temporal trends.

Experimental Section

Sample Sites. The samples analyzed are summarized in Figure 1. Nineteen contemporary sewage sludge samples were collected from 14 WWTPs in Catalonia from 1994 to 1998. These WWTPs are representative of rural, urban, and industrial areas. Twenty-four archived samples were acquired from 15 WWTPs in Catalonia from 1979 to 1987 and stored in sealed containers after being air-dried. Some of them were employed for a long-term agricultural experiment. These were used recently to quantify the inputs of PCDDs, PCDFs, and PCBs to agricultural soils in sewage sludge and to investigate their effects on the soil (*21*).

Extraction and Cleanup. The samples were air-dried and manually ground before extraction. Ten gram dry weight (d.w.) sludge samples were spiked with a mixture of 15 $^{13}C_{12}$-labeled 2378-substituted isomers (Chemsyn Science Laboratories, Lenexa, USA) and extracted in a Soxhlet apparatus for 48 h with toluene of pesticide grade (Merck). After extraction, the crude extracts were transferred to hexane and treated with concentrated H_2SO_4, followed by purification via a 3-stage (multilayer silica, Florisil and basic alumina) open column chromatographic procedure. 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 (*21, 22*).

Instrumental Analysis. Purified PCDD/PCDF extracts were analyzed by HRGC−HRMS on a Fisons 8060 gas chromatograph fitted with a DB-5 (J&W Scientific, CA) fused-silica capillary column (60 m × 0.25 mm ID, 0.25 μm film thickness) coupled to an AutoSpec-Ultima (VG, 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 based on the relative response factors (RRFs) previously obtained from five standard solutions (CSL) (*21, 23*). The data achieved were evaluated employing defined analytical criteria. The acceptance criteria for data include chlorine isotope ratio within ±15% of the correct ratio, peak maxima retention time within 2 s, and peak responses at least 3 times the background noise level.

Results and Discussion

Contemporary Sludge Samples. The PCDD and PCDF concentrations in the 19 sewage sludges analyzed by HRGC−HRMS are given in Table 1. Dioxin and furan recovery values, ranging from 76% to 108%, showed a satisfactory analysis procedure.

To normalize concentrations and the toxicity of the different PCDD and PCDF congeners, international toxicity equivalent factors (I-TEFs) (*24*) were used to calculate the

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FIGURE 1. WWTP sludge sampling locations, Catalonia (Spain).

international toxicity equivalent (I-TEQ) for the samples. The I-TEQ values represent the equivalent concentration of 2378-TCDD. Total I-TEQ values for the samples analyzed ranged from 7 to 160 pg/g, with a mean value of 55 pg/g and a median value of 42 pg/g. The variation in the I-TEQ concentration may be attributed to varying loads during the sample collection period at the different sewage treatment plants. It should be point out that with the exception of the sewage sludges from Igualada, Terrassa, and Vic, the sludges produced in the other WWTPs studied were applied to land for agricultural purposes. In 1992, a limit value of 100 pg of I-TEQ/g of dry matter for PCDDs/PCDFs in sludges used in German agriculture was established (*25*). From the 19 samples analyzed in our laboratory, four exceeded this limit (Manresa X-96, Solsona 1996, Tossa, and Vilafranca), which represents 21% of the samples studied.

The concentrations of PCDDs were higher than those of PCDFs, with the ratio $R_{(\text{I-TEQ PCDDs/I-TEQ PCDFs})} > 1$ for all the samples with the exception of Manresa XI-94, St. Fruitós, and Vilafranca. The values >1 ranged between 1 and 25, with a mean value of 5, which matched reasonably well those observed by Rappe et al. (*26*). A general rise in concentration with an increasing degree of chlorination can be observed, OCDD being the predominant congener. This is consistent with findings for sewage sludges (*5, 11, 27−30*). Our samples were dominated by octa- and hepta-CDDs. In fact, of the samples with $R > 1$, the contribution of the octa- and hepta-CDDs to the total I-TEQ ranged from 8% (Tossa) to 78% (Solsona, 1997), with a median contribution of 43% from these congeners.

In Table 2 we present an estimate of the PCDD and PCDF accumulated in the total sewage sludges produced in Catalonia. A quantity of 8 g of I-TEQ/year is only an approximate value, based on the analysis of sewage sludge samples which represent 12% of the total production. However, the WWTPs selected for this study are representative of the different types of WWTPs in Catalonia. The data of sewage sludge production for each location studied corresponded to 1997, while the total sewage sludge production is an estimate for the year 2000.

Archived Sludge Samples. The concentrations of dioxins and furans in the 24 archived sewage sludge samples analyzed are given in Table 3. The recovery values were satisfactory and ranged from 63% to 104%. Total I-TEQ values ranged from 29 to 8300 pg/g with a mean value of 620 pg/g and a median value of 110 pg/g. Fifty-eight percent of the archived samples analyzed exceeded the limit value set at 100 pg of

TABLE 1. Concentrations of PCDDs and PCDFs (expressed in pg/g dry weight) in 19 Contemporary Sewage Sludge Samples Studied

	Balaguer V-95	Figueres XI-97	La Bisbal XI-94	Igualada VII-98	Manresa XI-94	Manresa I-96	Manresa VII-96	Manresa X-96	Manresa XII-96	Olot VII-98	Roses XI-97	Sabadell VI-98	St. Fruitós XII-96	Solsona 96	Solsona VI-97	Terrassa V-98	Tossa XI-97	Vic I-94	Vilafranca III-97
2378-TCDD	1.5	0.8	0.4	ND	ND	1.0	4.6	1.5	NQ	0.5	1.9	1.1	0.6	0.6	NQ	1.0	3.8	0.5	8.7
12378-PeCDD	3.1	5.7	2.7	NQ	2.5	1.8	3.7	3.3	2.9	2.2	3.9	2.8	1.3	ND	1.0	1.7	71	0.7	29
123478-HxCDD	2.6	3.7	2.9	0.4	ND	1.3	4.5	NQ	5.8	0.9	3.2	1.3	1.8	ND	2.1	2.9	140	1.0	20
123678-HxCDD	2.5	15	35	4.5	31	48	200	360	200	5.8	10	11	44	98	14	35	230	13	34
123789-HpCDD	9.1	11	13	2.0	9.6	22	80	100	73	4.6	11	6.9	13	420	5.5	17	620	3.7	63
1234678-HpCDD	750	300	1100	140	840	1200	1600	7100	3300	95	170	200	350	4000	960	590	1000	410	290
OCDD	5700	2000	4600	2500	5100	7800	6000	15000	9600	1100	1600	2000	1000	19000	4700	3800	3500	4900	1800
2378-TCDF	8.9	27	5.5	3.6	130	80	38	37	37	5.8	7.2	7.5	85	4.9	1.6	72	21	8.1	82
12378-PeCDF	1.0	2.9	1.2	0.5	15	34	9.8	6.9	16	1.5	1.7	1.3	63	ND	0.4	8.2	2.5	0.7	30
23478-PeCDF	1.6	11	1.5	1.2	13	25	11	11	12	2.1	2.6	2.8	39	ND	1.1	32	1.9	2.0	55
123478-HxCDF	3.3	11	3.4	2.5	19	29	16	17	17	4.2	4.3	7.4	51	ND	2.3	13	9.4	3.5	150
123678-HxCDF	2.5	5.4	2.2	0.7	5.3	7.9	4.2	4.4	5.2	1.9	2.1	2.7	12	130	0.7	6.9	5.0	1.5	52
234678-HxCDF	2.6	7.2	2.7	2.6	5.1	7.5	5.8	5.2	6.8	4.4	2.8	3.8	13	5.1	2.0	12	7.0	1.8	76
123789-HxCDF	0.4	0.2	0.4	NO	0.6	6.8	2.2	3.7	0.8	ND	0.1	0.2	1.1	ND	NQ	0.4	0.6	0.6	5.8
1234678-HpCDF	26	28	30	56	32	77	51	77	56	27	37	100	35	ND	21	160	55	11	230
1234789-HpCDF	1.9	2.3	1.5	1.2	3.4	8.0	3.7	5.7	5.5	1.5	1.3	5.3	2.4	ND	1.5	5.6	3.7	11	230
OCDF	66	43	47	170	74	940	110	200	120	43	45	900	28	330	38	790	30	27	170
I-TEQ(PCDDs)	20	12	22	4.6	19	29	57	140	72	4.7	9.6	8.4	12	110	17	17	150	12	40
I-TEQ(PCDFs)	3.0	11	2.6	2.3	24	29	13	14	14	3.1	3.5	5.6	39	14	1.5	29	6.0	2.7	69
R(PCDDs/Fs)	6.7	1.0	8.6	2.0	0.8	1.0	4.3	9.9	5.0	1.5	2.8	1.5	0.3	7.8	12	0.6	25	4.3	0.6
I-TEQ(Total)	23	23	24	6.9	43	58	70	150	86	7.8	13	14	51	130	18	46	160	14	110

[a] ND = not detected. NQ = not quantified (*Rs/n* <3).

TABLE 2. Estimate of the PCDDs and PCDFs Accumulated in Sewage Sludge Produced in Catalonia (Spain)

WWTP	inhabitant eq.	sludge volume (tonnes (d.w.)/year)	pg of I-TEQ/g	mg of I-TEQ/year
Balaguer	18682	188	22.90	4.29
La Bisbal	9393	202	24.49	4.95
Figueres	62042	859	22.54	19.38
Igualada	287477	5735	6.89	39.52
Manresa	134177	2148	81.15[a]	174.31
Olot	69369	631	7.76	4.90
Roses	31733	392	13.07	5.12
Sabadell	202078	2528	13.98	35.35
St. Fruitós	27000	695	50.78	35.29
Solsona	10899	2378	72.38[a]	172.12
Terrassa	340726	5735	46.15	264.67
Tossa	10059	162	157.91	25.63
Vic	318073	7249	14.48	104.97
Vilafranca	67283	1117	108.04	120.66
Σ14 WWTPs	1588991	30020		1011.15
Catalonia[b]	8630531	246434		8300.54

[a] Mean value from the different determinations. [b] Estimate to year 2000.

I-TEQ/g for agricultural purposes. The total I-TEQ values in the archived samples were higher than those measured in contemporary sludges, with an increase of 11.3 and 2.6 the in mean and median values, respectively.

The levels detected in the contemporary sewage sludge study were substantially lower than the mean and median levels reported for the archived sewage sludge study. It cannot be established from our limited study whether this difference reflects a general decline in PCDDs and PCDFs in sewage sludges of Catalonia over the past decade or whether the lower levels observed here simply reflect the characteristics of the WWTPs surveyed here. Thus, the study was performed by analyzing some samples from the same WWTP at different times. In 5 out of 7 samples the PCDD and PCDF concentrations show a marked decline: an approximately 6-fold decrease for Roses, 15-fold for Figueres, 35-fold for Manresa, 132-fold for Olot, and 1203-fold for Igualada. The reduction was more pronounced in the samples with high levels in 1979/87 than in those with low levels. No variations could be observed for Tossa, and a small increase was detected in the contemporary sample for Vilafranca. These results, therefore, show a fall in contemporary sewage sludge PCDD and PCDF concentrations since the 1980s.

The concentrations of the sum of PCDDs were higher than those of the sum of PCDFs, with the ratio $R_{(\text{I-TEQ PCDDs/I-TEQ PCDFs})} > 1$ for all the samples. The values ranged between 3 and 120 (with a mean value of 15), which were higher than those observed for contemporary samples. A general rise in concentration with an increasing degree of chlorination was observed, with OCDD being the predominant congener. The samples were dominated by octa- and hepta-CDDs. In fact, the contribution of the octa- and hepta-CDD to the total I-TEQ ranged from 12% (Igualada) to 80% (Figueres 1986), with a median contribution of 64% from these congeners. It should be pointed out that the lower I-TEQ values in contemporary samples are not due to a general decrease in each congener group, but mainly to smaller concentrations of HxCDDs, HpCDDs, and OCDD (Figure 2). The levels of the homologous groups, i.e., PCDFs, TCDDs, and PeCDDs, do not vary very much in the archived and contemporary samples. Therefore, to detect changes in PCDD and PCDF sources to the environment over time, it is necessary to study sources that lead to an increase in the levels of HxCDDs, HpCDDs, and OCDD, in which the PCP products are prominent. PCP and its derivates (NaPCP and PCPL) contain PCDDs and PCDFs (predominantly HpCDDs and OCDD) as impurities and probably represent an im-

TABLE 3. Concentrations of PCDDs and PCDFs (expressed in pg/g dry weight) in 24 Archived Sewage Sludge Samples Studied

	Besós 1979	Bogatell 1979	Blanes 1979	Castelldefels 1987	Figueres 1979	Figueres 1984	Figueres 1985	Figueres 1986	Figueres 1987	Girona 1987	Igualada 1987	Manresa 1987	Olot 1979	Portbou 1979	Reus 1979	Reus 1979	Roses 1979	Roses 1982	Roses 1983	St. Feliu 1987	Tossa 1983	Tossa 1987	Vilafranca 187
2378-TCDD	0.6	17	0.6	0.8	11	1.0	1.9	0.2	0.8	NQ	1.4	1.3	NQ	2.3	0.6	0.7	4.0	1.0	0.8	0.2	NQ	0.6	NQ	ND
12378-PeCDD	2.0	33	0.6	4.7	33	9.1	8.3	9.5	6.1	7.7	2.9	52	20	21	3.4	2.7	8.4	3.0	3.9	3.5	2.6	4.2	4.6	ND
123478-HxCDD	21	29	30	5.0	48	26	7.1	10	9.2	8.9	4.2	NQ	120	150	7.2	5.0	6.5	5.9	12	4.0	9.3	3.8	3.8	2.5
123678-HxCDD	330	160	26	360	770	330	110	210	250	180	60	55000	5500	1800	59	72	57	58	170	47	130	68	120	47
123789-HxCDD	140	160	8.1	100	190	130	53	91	53	66	24	17000	1100	290	29	28	29	25	91	28	45	40	43	19
1234678-HpCDD	6000	2700	1100	3600	45000	12000	4500	6400	15000	5800	1400	87000	180000	54000	2600	3700	2100	2300	5000	1700	2200	3400	6800	2600
OCDD	54000	14000	6400	16000	100000	43000	21000	26000	49000	22000	14000	140000	270000	190000	14000	21000	30000	18000	18000	19000	25000	16000	30000	18000
2378-TCDF	15	26	7.2	15	240	78	43	60	48	54	7.6	35	41	14	13	13	33	35	19	28	18	25	20	11
12378-PeCDF	1.4	11	2.0	3.2	31	13	15	8.8	3.5	6.5	1.1	20	4.9	7.5	1.6	2.7	5.8	6.1	2.9	4.0	3.8	1.1	2.3	1.7
23478-PeCDF	5.8	12	3.5	5.1	72	27	16	20	7.9	14	4.2	33	14	7.7	3.4	6.2	13	16	4.1	6.3	6.7	5.2	3.9	2.7
123478-HxCDF	10	34	3.3	8.5	120	46	25	28	16	21	13	70	140	74	6.3	9.9	17	33	19	13	12	17	9.1	8.0
123678-HxCDF	3.2	16	1.4	3.2	56	27	12	17	7.3	8.4	4.9	41	31	36	3.4	3.5	7.6	9.3	6.1	5.9	5.8	4.7	4.6	3.1
234678-HxCDF	8.5	11	2.5	5.3	75	39	15	21	10	11	6.3	170	99	130	3.1	4.9	9.0	13	11	8.7	7.9	9.6	7.0	4.2
123789-HxCDF	0.1	0.5	ND	NQ	1.8	1.5	NQ	NQ	0.3	0.5	0.3	2.8	3.1	3.0	ND	NQ	NQ	0.3	0.2	0.1	NQ	NQ	1.2	NQ
1234678-HpCDF	44	69	26	56	160	550	100	170	170	82	67	1800	2300	1900	75	57	120	130	78	120	110	100	84	50
1234789-HpCDF	2.7	7.2	1.6	2.9	41	28	6.3	10	9.1	4.8	5.7	30	390	140	4.2	4.3	6.8	9.3	2.8	6.0	5.8	3.3	4.5	5.9
OCDF	9.5	52	48	50	670	620	190	240	400	120	140	650	1500	2800	130	3.8	190	240	78	160	130	94	190	250
I-TEQ(PCDDs)	160	110	25	100	680	220	88	130	240	110	40	8200	2600	970	52	70	69	53	98	46	67	64	120	50
I-TEQ(PCDFs)	7.2	16	3.6	6.6	89	40	19	25	14	18	6.2	69	110	53	5.3	7.0	15	19	8.5	10	9.2	9.5	7.4	4.9
R(PCDDs/FS)	23	6.8	6.9	16	7.6	55	4.6	5.0	16	6.1	6.4	120	24	18	9.9	10	4.6	2.8	11	4.4	7.3	6.8	16	10
I-TEQ(Total)	170	120	29	110	770	260	110	150	250	130	46	8300	2700	1000	57	77	84	72	110	56	76	74	130	55

[a] ND = not detected. NQ = not quantified ($Rs/n < 3$).

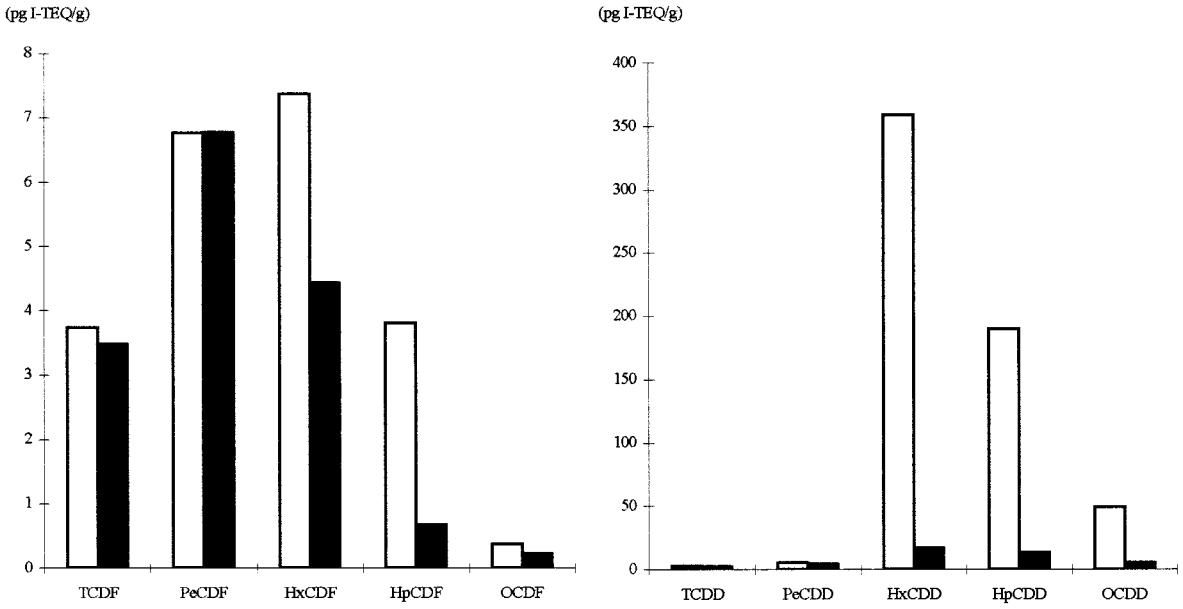

FIGURE 2. Congener profile distribution (obtained with mean values from the different determinations) for the archived (white) and contemporary (black) sewage sludge samples.

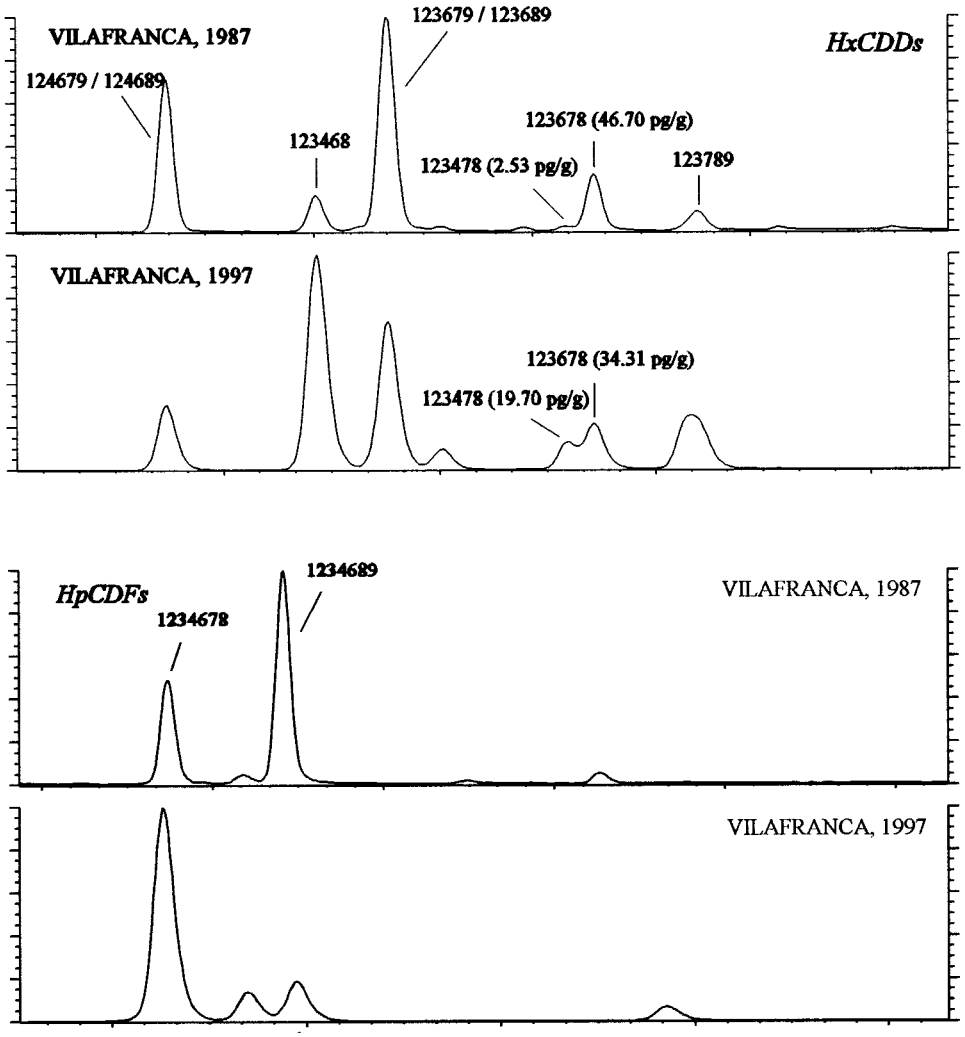

FIGURE 3. Isomeric distribution changes in HxCDD and HpCDF patterns observed between archived and contemporary sewage sludge from Vilafranca.

portant PCDD and PCDF source for sewage sludges. PCP has been widely used since the 1930s. Owing to the health and environmental hazards associated with PCP, stringent controls on its production and use have been set up. Many

TABLE 4. Variations in PCDD and PCDF Concentrations and in 123678-HxCDD:123478-HxCDD, 1234678-HpCDF:HpCDFs, and 124689-HxCDFs Ratios, between Archived and Contemporary Sewage Sludges Sampled in the 1980s and 1990s

	pg of I-TEQ/g		123678:123478-HxCDD ratio		1234678:total-HpCDFs ratio		124689:total-HxCDFs ratio	
	archived	contemp.	archived	contemp.	archived	contemp.	archived	contemp.
Figueres	277.06[a]	22.54	18.5[a]	4.0	0.3[a]	0.5	0.19[a]	0.07
Igualada	8287.59	6.89	∞[b]	11.9	0.4	0.6	0.19	0[c]
Manresa	2726.22	81.15[a]	46.6	39.3[a]	0.1	0.3[a]	0.51	0.18[a]
Olot	1027.80	7.76	12.1	6.8	0.3	0.6	0.42	0.09
Roses	78.17[a]	13.07	11.8[a]	3.2	0.4[a]	0.6	0.16[a]	0.10
Tossa	99.42[a]	157.91	24.8[a]	1.6	0.3[a]	0.6	0.19[a]	0.07
Vilafranca	55.46	108.04	18.5	1.7	0.2	0.6	0.26	0.01

[a] Mean value from different determinations. [b] 123478-HxCDD was not quantified (*Rs/n < 3*) for this sample. [c] 124689-HxCDF was not quantified (*Rs/n < 3*) for this sample.

developed countries have banned the use of PCP (Sweden in 1978, Germany in 1990, and Denmark in 1996 (*31*)) or severely restricted its use for many years (e.g., Finland, Canada). Since 1991, EU legislation has limited the use and application of PCP-based products in order to minimize human exposure (EEC 91/179/ EEC). Other possible important sources of contamination of PCDFs and PCDDs, such as the discharges from PVC manufacture or the MSWI emissions, are not taken into account as there is no industrial plant of this type in the vicinity of the locations studied. The emissions from other combustion activities, such as leaded gasoline-powered vehicles and home heating combustion sources (wood, coal, and oil), are known to give a distinctive homologue pattern with predominance of TCDFs and PeCDFs. As can be seen in Figure 2, no significant differences were observed between TCDFs and PeCDFs from the archived and contemporary samples. It should be pointed out that the incidence of home heating combustion sources is not important in tempered countries such as Spain. Moreover, a possible decline in PCDDs and PCDFs levels due to the use of unleaded gasoline cannot be observed in the contemporary samples studied because this use is being introduced only in the last few years in Spain.

The PCP influence could be studied by the differences observed in the isomeric distributions in sewage sludge samples from the same WWTP at different times, e.g., Figure 3 shows the HxCDD and HpCDF patterns for the archived and contemporary sewage sludge from Vilafranca. The HxCDD pattern in the archived sample shows that of all the contributions, 123679/123689 is the largest followed by 124679/124689. However, the contemporary sample accounts for the largest contribution of 123468 and a low amount for 124679/124689. There are also some differences regarding the 2378-substituted isomers (123478, 123678, and 123789). The ratio of 123678-HxCDD:123478-HxCDD is a useful marker for technical mixtures of PCP, typically being ≥100 (*32*). This ratio has also been found to be a useful indicator of PCP influence on the environment. This ratio should, therefore, show a sharp increase if the rise in PCDD and PCDF levels in sludge samples is attributed to the use of PCP. This ratio decreased, from a value of about 19 in the early Vilafranca sample to 2 between 1979 and 1997, suggesting that PCP is a possible source of PCDDs and PCDFs in the archived sewage sludge sample. In Table 4, we present the 123678:123478 ratio for the seven WWTPs sampled in the 1980s and 1990s. With the exception of Manresa, this ratio is considerably lower for the archived samples than for the contemporary samples. During this time, the levels of 123478 diminished for the Figueres, Manresa, Olot, and Roses samples, despite being absent in most technical PCP products. This suggests that "pure" PCP is unlikely to be the dominant source of PCDDs and PCDFs in these sewage sludge samples.

As for the HpCDF patterns, changes could also be observed between the archived and the contemporary samples (Figure 3). In the archived sample from Vilafranca, 1234689 is the predominant isomer, whereas in the contemporary sample, 1234678 presented the highest contribution. A low ratio of 1234678-HpCDF to total HpCDFs is a strong indication of PCP contamination (*6*). In the samples from the 1980s, the 1234678-HpCDF to total HpCDFs ratio was lower than that of the samples of the 1990s (Table 4).

A further PCP "signature" is the 124689-HxCDF to total HxCDFs ratio, which is significantly higher in PCP- and PCP-contaminated matrixes (*32*−*34*). In Table 4, we present the ratio obtained for the seven WWTPs sampled in the 1980s and 1990s. This ratio is considerably higher for the archived samples than for the contemporary samples.

Our study of the isomeric distribution suggests a major input because of the use of pentachlorophenol in archived samples. The lower levels detected in the contemporary samples could reflect a general decline in PCDD/F inputs to the environment, owing to tighter controls on PCP use and disposal.

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Literature Cited

(1) Commission of the European Communities. *Council Directive concerning Urban Wastewater Treatment*; Official Journal of the European Communities L135/40−52.
(2) Tiernan, T. O.; Garrett, J. H.; Solch, J. G.; VanNess, G. F.; Wagel, D. J.; Rukunda, F. *Organohalogen Compd.* **1997**, *32*, 98−102.
(3) Gihr, R.; Klöpffer, W.; Rippen, G.; Partscht, H.; Stoll, U.; Müller, J. *Chemosphere* **1991**, *23*, 1653−1659.
(4) Hagenmaier, H.; She, J.; Benz, T.; Dawidowski, N.; Düsterhöft, L.; Lindig, C. *Chemosphere* **1992**, *25*, 1457−1462.
(5) Broman, D.; Näf, C.; Rolff, C.; Zebühr, Y. *Chemosphere* **1990**, *21*, 1213−1220.
(6) Sewart, A.; Harrad, S. J.; McLachlan, M. S.; McGrath, S. P.; Jones, K. C. *Chemosphere* **1995**, *30*, 51−67.
(7) Rappe, C.; Andersson, R.; Kalaganis, G.; Bonjour, R. *Organohalogen Compd.* **1994**, *20*, 79−84.
(8) Heister, E.; Bruckmann, P.; Bohm, R. *Organohalogen Compd.* **1995**, *24*, 147−152.
(9) Kjeller, L. O.; Jones, K. C.; Johnston, A. E.; Rappe, C. *Environ. Sci. Technol.* **1996**, *30*, 1398−1403.
(10) Kjeller, L. O.; Rappe, C. *Environ. Sci. Technol.* **1995**, *29*, 346−355.
(11) Hagenmaier, H.; Brunner, H.; Haag, R.; Berchtold, A. *Chemosphere* **1986**, *15*, 1421−1428.
(12) Beurskens, J. E. M.; Mol, G. A. J.; Barreveld, H. L.; van Munster, B.; Winkels, H. J. *Environ. Toxicol. Chem.* **1993**, *12*, 1549−1566.
(13) Rappe, C.; Kjeller, L. O. *Organohalogen Compd.* **1994**, *20*, 1−7.
(14) Fürst, P.; Wilmers, K. *Organohalogen Compd.* **1995**, *26*, 101−104.
(15) Papke, O.; Ball, M.; Lis, A. *Chemosphere* **1994**, *29*, 2355−2360.
(16) Noren, K. *Sci. Total Environ.* **1993**, *139/140*, 347−355.

(17) Liem, A. K. D.; Albers, J. M. C. *Organohalogen Compd.* **1995**, *26*, 69−74.
(18) Lamparski, L.; Nestrick, T.; Stenger, V. *Chemosphere* **1984**, *13*, 361−365.
(19) Jones, K. C.; Sewart, A. P. *Dioxins and furans in sewage sludges: a review of their ocurrence and sources in sludge and of their environmental fate, behaviour and significance in sludge-amended agricultural systems*; Department of the Environment Report EPG 1/9/13; 1995.
(20) Rappe, C.; Andersson, R.; Studer, C.; Karlaganis, G. *Organohalogen Compd.* **1997**, *33*, 82−87.
(21) Eljarrat, E.; Caixach, J.; Rivera, J. *Environ. Sci. Technol.* **1997**, *31*, 2765−2771.
(22) Casanovas, J.; Muro, R.; Eljarrat, E.; Caixach, J.; Rivera, J. *Fresenius J. Anal. Chem.* **1994**, *348*, 167−170.
(23) Eljarrat, E.; Casanovas, J.; Muro, R.; Huguet, X.; Caixach, J.; Rivera, J. *Quím. Anal.* **1995**, 14, 89−95.
(24) NATO/CCMS, 1988. *International Toxicity Equivalent Factor (I-TEF). Method of risk assessment for complex mixtures of dioxins and related compounds. Pilot study on international information exchange on dioxins and related compounds;* Report no. 176.
(25) Klärschlammverordnung-Abfklärv vom 15 April 1992. Bundesgesetzblatt, Jahrgang 1992, Teil I, S. 912−934.
(26) Rappe, C.; Andersson, R.; Bonner, M. S.; Cooper, K. R.; Fiedler, H.; Howell, F. G.; Lau, C. *Organohalogen Compd.* **1996**, *28*, 105−110.
(27) Rappe, C.; Kjeller, L. O.; Andersson, R. *Chemosphere* **1989**, *19*, 13−20.
(28) Naf, C.; Broman, D.; Ishaq, R.; Zebuhr, Y. *Chemosphere* **1990**, *20*, 1503−1510.
(29) McLachlan, M. S.; Reissinger, M. *Organohalogen Compd.* **1990**, *1*, 577−580.
(30) Nestrick, T.; Lamparski, L. *Chemosphere* **1983**, *12*, 617.
(31) Anon, Danes cleared to keep PCP ban despite conflict with EC rules; ENDS Report 254, March 1996.
(32) Hagenmaier, H.; Brunner, H. *Chemosphere* **1987**, *16*, 1759−1764. Ryan, J. J.; Lizotte, R.; Lewis, D. *Chemosphere* **1987**, *16*, 1989−1996. Harrad, S. J.; Malloy, T. A.; Ali Khan, M.; Goldfarb, T. D. *Chemosphere* **1991**, *23*, 181−191.

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