

LEVELS IN ABIOTIC COMPARTMENTS

PCDD/PCDF IN THE VICINITY OF A HAZARDOUS WASTE INCINERATOR IN CATALONIA, SPAIN. I. LEVELS IN SOILS

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Introduction

Waste incineration (hazardous, medical and municipal) is a widely used method of waste management. However, in many countries there is a great concern in relation to waste incinerators taking into account the proved relationship with emission of atmospheric toxic contaminants such as metals and polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs). Nevertheless, other many different activities^{1,2} are also known sources of PCDDs and PCDFs emission.

In 1996, the construction of the first and only hazardous waste incinerator (HWI) in Spain was initiated. Regular operations started in 1999. Generally, evaluation of HWI stack emissions have been focused on heavy metals, semivolatile and volatile compounds³. In spite of the fact that PCDD/F emissions from HWI are about three of four orders of magnitude lower than PCDD/F emissions reported from municipal waste incinerators⁴, because of the public and scientific concern, especial attention has been paid to these pollutants. In response to this concern, a wide environmental program was designed in order to assess the impact of PCDD/PCDF emissions from the new HWI on the neighbourhood, as well as to establish the potential health risks on the population living in the vicinity of the facility.

Once emitted into the atmosphere, PCDD/Fs are dispersed throughout the environment, and because their semivolatile and hydrophobic properties they accumulate in organic rich media such as soils. Since atmospheric deposition is the main mean of supplying PCDD/Fs to soils, they are widely used in environmental programs as an accumulative monitor of long-term exposure to PCDD/Fs. In 1996, the baseline concentrations of PCDD/Fs were determined in soil and vegetation samples collected near to the HWI under construction⁵⁻⁷. In order to assess the temporal variation in the levels of PCDD/Fs in environmental matrices, an additional baseline study was done in 1998⁸. In this survey, soil and herbage samples were again collected at the same sampling points and the levels of PCDD/Fs were determined. In 2001, two years after the plant initiated regular operations, PCDD/Fs were again determined in soil and herbage samples collected in the vicinity of the plant. A companion paper shows the results in vegetation samples⁹.

Methods and Materials

In April 2001, three years after the last sample collection, a third sampling was carried out. Forty soil samples were collected in the same points in which samples had been taken in the previous surveys⁵⁻⁷. Thirty samples corresponded to rural soils, while the remaining 10 corresponded to urban soils. At each sampling site, a minimum of 500 g of the upper 5 cm of soil were taken. Duplicate samples were kept to be used if necessary. Samples were sieved through a 2-mm mesh screen to obtain

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an homogenous grain distribution. Determination of dry matter content was achieved by drying subsamples (1-3 g) at 130°C overnight. About 30 g (dry weight) were used for analysis.

The extraction and clean-up procedures, as well as the analytical determination of PCDD/Fs were carried out as previously reported⁸. The instrumental analysis was performed by HRGC/HRMS in a CE 8000 gas chromatograph coupled to an AutoSpec Ultima mass spectrometer, operating in EI ionization (32 eV) at 10000 resolving power. The samples were analysed on a SPB-5 (60 m x 0.25 mm x 0.25 mm) capillary column. Monitored masses were those proposed by EPA 1613.

The 2,3,7,8-TCDD toxic equivalents (I-TEQ) were calculated using the NATO/CCMS factors. When a result was under the detection limit, to calculate mean and I-TEQ values the congener was assumed to be present at one-half of the method detection limit (MDL). A multivariate analysis of the results was done. Data matrices were evaluated through Principal Component Analysis (PCA). All calculations were performed using the SPSS-10.0 statistical package.

Results and Discussion

Table 1 summarizes the individual concentrations of PCDD/Fs found in the 40 soil samples collected near the HWI, as well as the levels found in the 1998 survey⁷. For each sample, the percentages of temporal variation of the I-TEQ values are also shown.

In the 1996 survey⁶, PCDD/Fs concentrations ranged from 0.13 to 24.20 ng I-TEQ/kg (dry matter), with median and mean values of 0.67 and 1.68 ng I-TEQ/kg (dry matter), respectively. In the 1998 survey⁸, PCDD/F concentrations ranged from 0.12 to 17.20 ng I-TEQ/kg (dry matter), with a median value of 0.75 ng I-TEQ/kg and a mean value of 1.59 ng I-TEQ/kg (dry matter). In the present study, PCDD/F concentrations ranged from 0.34 to 30.40 ng I-TEQ/kg (dry matter), with median and mean values of 0.97 and 2.04 ng I-TEQ/kg (dry matter), respectively. From 1998 to 2001, PCDD/F levels increased in 20 of the 40 samples and they decreased in 19. One sample did not show any variation. Although the median value was 29.3% higher in 2001 than in 1998, this difference did not result to be statistically significant.

Most tetra- to octa-PCDD/Fs were detected in all samples. In the 1998 survey, 2,3,7,8-TCDD, the most toxic congener, was identified in 20 of the 40 samples (detection limit: 0.05 ng/kg dry matter), with 0.50 ng/kg being the highest concentration found, 0.10 ng/kg the mean value and 0.08 the median value. In the present study, 2,3,7,8-TCDD was only detected in 2 of the 40 samples, whose levels were 0.27 and 0.85 ng/kg (dry matter). In turn, in the 1998 survey OCDD concentrations ranked between 4.07 and 527 ng/kg, while in the current study they ranked between 2.53 and 819 ng/kg. The PCDD/F congener profiles for the samples collected in 1998 and again in 2001 are depicted in Figure 1. On the other hand, when a multivariate analysis (PCA) was applied to the data, the scatterplot of the component scores on both principal components showed that most samples are located in a main cluster, with only a few samples appearing as outliers (Figure 2).

The increase in the PCDD/Fs levels detected during the period 1998-2001 was not statistically significant ($p > 0.05$). It was of the same order of magnitude than that observed between the 2 baseline studies (1996 and 1998)^{7,8}. Soil is an accumulative matrix, and consequently, it would have been quite surprising if the current PCDD/F concentrations soils were at present lower than 3 years ago, taking into account that no significant modifications (reductions) of the diverse activities of the area, potentially emitting PCDD/Fs, have been reported. Anyhow, the current PCDD/F levels are relatively low in comparison with recent data from other places.

On the other hand, the global analysis of the current soil and vegetation^{7,8} data indicates that samples collected in urban or rural areas, which are potentially exposed to different PCDD/F sources (such as vehicle traffic, fires, pesticides, etc) show different PCDD/F congener profiles. The

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Table 1. PCDD/F concentrations (ng I-TEQ/kg dry matter) in soil samples collected in the vicinity of a new hazardous waste incinerator in 1998 and in 2001: Temporal variation.

Sample	Area	Soil			Sample	Area	Soil		
		1998	2001	Variation %			1998	2001	Variation %
E-1	R	1.22	0.60	-50.8	NO-5	R	0.66	0.61	-7.6
E-2	R	0.52	0.58	-11.5	NO-6	R	1.07	0.89	-16.8
E-3	R	0.41	0.67	63.4	NO-7	R	2.34	0.84	-64.1
E-4	R	0.65	0.58	-10.8	S-1	R	1.10	0.71	-35.5
E-5	R	5.11	8.66	69.5	S-2	R	1.02	1.21	18.6
E-6	R	0.40	1.22	205.0	S-3	R	0.75	0.97	29.3
E-7	R	0.12	0.65	441.7	S-4	R	0.45	1.07	137.8
E-8	U	1.99	1.33	-33.2	S-5	R	1.01	2.55	152.5
E-9	R	0.16	1.26	687.5	S-6	R	1.00	0.72	-28.0
N-1	R	0.34	0.97	185.3	S-7	R	0.35	0.84	140.0
N-2	R	0.23	0.39	69.6	S-8	R	1.94	0.97	-50.0
N-3	R	0.26	0.56	1.1	SV1	U	0.15	1.24	726.7
N-4	R	0.75	0.34	-54.7	SV2	U	2.00	2.55	27.5
N-5	R	0.13	1.15	784.6	SV4	U	3.43	2.02	-41.1
N-6	R	0.51	0.51	0.0	SV6	U	3.61	1.50	-58.4
N-7	R	0.60	0.52	-13.3	SV7	U	2.42	30.37	1154.9
NO-1	R	0.64	0.51	-20.3	SV8	U	17.20	1.24	-92.8
NO-2	R	0.22	1.12	409.1	SV9	U	3.06	1.03	-66.3
NO-3	R	0.43	0.41	-4.6	SV10	U	0.84	5.96	609.5
NO-4	R	3.68	0.52	-85.9	SV11	U	0.75	1.71	128.0

R = rural area; U = urban area.

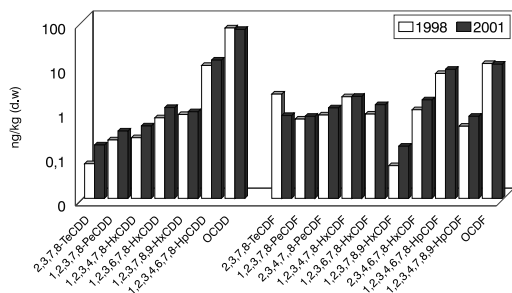


Figure 1. PCDD/F congener profiles in soil samples collected in 1998 and 2001 in the vicinity of a HWI.

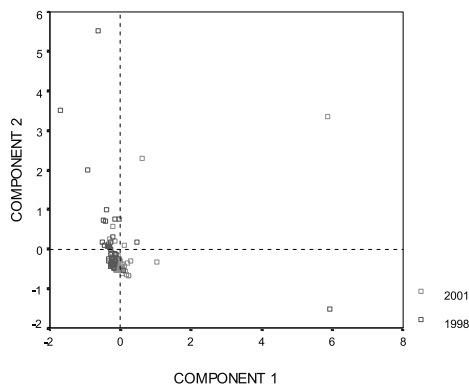


Figure 2. Principal component plot of soil samples collected in 1998 (n=40) and 2001 (n=40).

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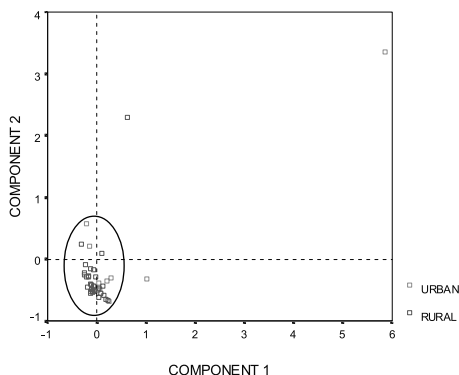


Figure 3. Principal component plot of soil samples collected in 2001 in urban (n=10) and rural (n=30) areas in the vicinity of a new HWI

multivariate analysis (PCA) of the data did not show significant differences in the PCDD/F congeners in soils between samples collected in urban and rural areas (Figure 3).

In summary, after three years of operation (including testing), it seems that the new HWI does not have a negative environmental impact in relation to the levels of PCDD/Fs in soils currently found, which should be a direct reflect of the atmospheric emission of PCDD/Fs from the plant.

Acknowledgements

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