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BASELINE CONTAMINATION ASSESSMENT FOR A NEW HAZARDOUS WASTE INCINERATOR IN CATALONIA, SPAIN. I. LEVELS OF PCDD/Fs IN SOIL SAMPLES

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Introduction

Combustion processes such as hazardous waste, medical waste, municipal solid waste, and sewage sludge incineration are among the major known sources of atmospheric contamination by polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs). However, in recent years it has been shown that PCDD/Fs are also generated during a wide range of different activities^{1,2}.

Recently, the first and only hazardous waste incinerator (HWI) in Spain began operation. Most evaluations of HWI stack emissions have focused on three classes of compounds: metals, semivolatile, and volatile compounds³. In relation to these pollutants the greatest amount of scientific and public attention has been given to one class of incinerator combustion products, PCDD/Fs. Therefore, although PCDDs and PCDFs have been detected frequently in HWI emissions at levels that are three or four orders of magnitude lower than emissions reported from municipal waste incinerators⁴, in the environmental monitoring program and the plant emission control program, measurements of the environmental levels of PCDD/Fs have been also included. Thus, during the period of construction of the facility, which is located in Constantí (Catalonia, Spain), baseline samples (soil and herbage) were collected in the vicinity of the new plant.

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. Atmospheric deposition is the main mean of supplying PCDD/Fs to soils, which are widely used in environmental programs as an accumulative monitor of long-term exposure to PCDD/Fs. In 1996, the concentrations of PCDD/Fs were determined in soil and vegetation samples collected near to the HWI under construction^{5,6}. To assess the temporal variation in the environmental levels of PCDD/Fs, in 1998 soil and herbage samples were again collected at the same sampling points and analyzed for the levels of PCDD/Fs. This paper presents the concentrations of PCDD/Fs in soils, as well as the comparison with those found in the 1996 survey. A companion paper shows the results in vegetation samples⁷.

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Methods and Materials

In April 1998, two years after the first sampling, 40 soil samples were collected in the same points in which samples had been taken in the 1996 survey⁵. Thirty samples corresponded to rural soils, while the remaining 10 corresponded to urban soils. At each sampling site, soils were taken from the upper 5 cm of solum. The sample amount consisted of a minimum of 500 g. Duplicate samples were kept to be used if necessary. Samples were sieved through a 2-mm mesh screen to obtain a more 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 reported⁵. 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 µm) 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-7.5 statistical software.

Results and Discussion

The individual concentrations of PCDD/Fs for the 40 soil samples (urban and rural) collected in 1998 near the new HWI are summarized in Table 1. The levels of PCDD/F found in the 1996 survey⁵, as well as the percentage of temporal variation of the I-TEQ values are also shown for each sample.

In the 1996 survey, PCDD/F concentrations in soils ranged from 0.11 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 present study, 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 1.56 ng I-TEQ/kg (dry matter). Between 1996 and 1998, PCDD/F levels decreased in 22 of the 40 samples, while they increased in the remaining 18 samples. However, no statistically significant differences were found for the 40 samples as a whole.

Most tetra- to octa-PCDD/Fs were detected in all samples. In the 1996 survey, 2,3,7,8-TCDD, the most toxic congener, was identified in 16 of the 40 samples (detection limit: 0.05 ng/kg dry matter), with 0.55 ng/kg being the highest concentration found. In the present study, 2,3,7,8-TCDD was detected in 20 of the 40 samples, with the highest level being 0.50 ng/kg (dry matter). The mean 2,3,7,8-TCDD concentrations were 0.06 ng/kg (median value, 0.02 ng/kg) and 0.10 ng/kg (median value, 0.08 ng/kg), respectively, for the 1996 and 1998 surveys. In turn, the rank of OCDD concentrations was between 4.10 and 1000 ng/kg (1996 survey), and 4.07 and 527 ng/kg (this study). The PCDD/F congener profiles for the samples collected in 1996 and again in 1998 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 most samples located in a main cluster with only a few samples appearing as outliers (Figure 2).

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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 before operation (1996 and 1998). Temporal variation.

		Soil					Soil		
Sample	Area	1996	1998	Variation %	Sample	Area	1996	1998	Variation %
E-1	R	1.35	1.22	-9.3	NO-5	R	0.53	0.66	25.7
E-2	R	0.55	0.52	-5.8	NO-6	R	1.11	1.07	-3.4
E-3	R	0.90	0.41	-54.2	NO-7	R	0.68	2.34	244.6
E-4	R	0.20	0.65	233.3	S-1	R	1.51	1.10	-27.2
E-5	R	0.70	5.11	625.9	S-2	R	0.17	1.02	510.8
E-6	R	0.73	0.40	-45.3	S-3	R	0.36	0.75	107.2
E-7	R	0.56	0.12	-78.7	S-4	R	0.13	0.45	243.5
E-8	U	1.05	1.99	90.4	S-5	R	0.19	1.01	420.6
E-9	R	0.63	0.16	-74.4	S-6	R	0.22	1.00	352.5
N-1	R	0.60	0.34	-43.7	S-7	R	8.40	0.35	-95.8
N-2	R	0.27	0.23	-14.5	S-8	R	0.59	1.94	229.9
N-3	R	0.59	0.26	-55.9	SV1	U	0.65	0.15	-77.0
N-4	R	1.26	0.75	-40.6	SV2	U	1.32	2.00	51.1
N-5	R	0.46	0.13	-71.7	SV4	U	2.24	3.43	53.5
N-6	R	0.37	0.51	60.4	SV6	U	1.59	3.61	127.5
N-7	R	0.33	0.60	82.7	SV7	U	3.88	2.42	-37.7
NO-1	R	0.68	0.64	-5.7	SV8	U	3.23	17.20	432.8
NO-2	R	0.36	0.22	-38.5	SV9	U	24.20	3.06	-87.4
NO-3	R	0.67	0.43	-35.8	SV10	U	1.09	0.84	-22.7
NO-4	R	0.81	3.68	354.3	SV11	U	1.23	0.75	-39.0

R= rural area; U= urban area.

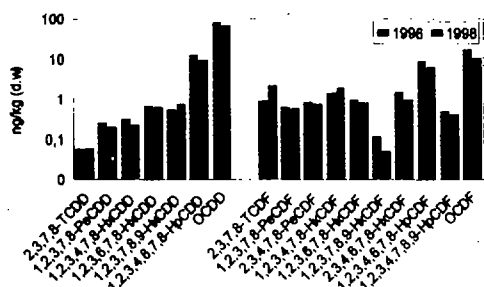


Figure 1. PCDD/F congener profiles in soil samples collected in 1996 and 1998 in the vicinity of a new HWI before operation.

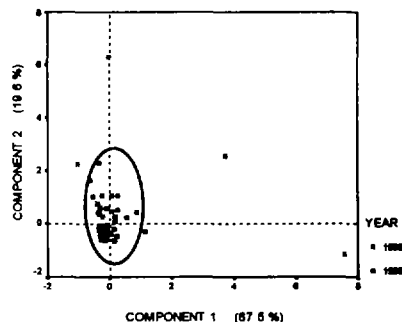


Figure 2. Principal component plot of soil samples collected in 1996 (n=40) and 1998 (n=40).

Taking into account that one of the largest petrochemical complex in southern Europe is located close to the area here examined, the current levels of PCDD/Fs are relatively low compared with those summarized in a recent overview on the status and regulatory aspects of dioxins and related compounds⁸. Mean PCDD/F concentrations (I-TEQ) in rural soil samples from five countries were the following: Canada, 1-330 ng/kg (dry matter); Germany, 2-5 ng/kg (dry matter); Japan, 1-65 ng/kg (dry matter); the Netherlands, 1-20 ng/kg (dry matter) and USA 8 ng/kg (dry matter). The low organic carbon content of the soils here examined could explain these comparatively low levels.

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A global analysis of the current soil and vegetation⁷ data indicates that samples collected in urban or rural areas, which are potentially exposed to different PCDD/F sources (as can be vehicle traffic, pesticides, etc), can show different PCDD/F congener profiles. Although in general terms, the 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), two different clusters were identified in herbage samples⁷. Therefore, it can be concluded that punctual sources of PCDD/Fs affected in a greater manner vegetation than soils.

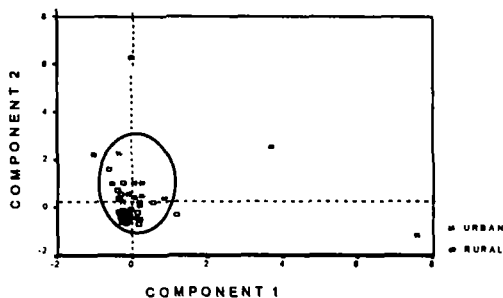


Figure 3. Principal component plot of soil samples collected in 1996 and 1998 in urban (n=20) and rural (n=60) areas in the vicinity of a new HWI.

According to the present and the previous levels of PCDD/Fs in soils, the area under potential influence of the new HWI shows a rather low contamination by these compounds. The current data will be useful to determine the environmental impact of the HWI in future assessments of the plant.

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