

Monitoring PCDD/Fs in soil and herbage samples collected in the neighborhood of a hazardous waste incinerator after five years of operation

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Introduction

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) are among the most dangerous environmental pollutants, usually generated during combustion processes¹. Until recently, waste incineration was widely referenced as one of the most important sources of PCDD/F release to the atmosphere.

In 1999, the only hazardous waste incinerator (HWI) in Spain began regular operations. This facility is placed in Tarragona, Catalonia. The presence of this HWI, as well as that of a municipal solid waste incinerator (MSWI) at a few kilometers, increased the concern of the public opinion in relation to the potential toxic emissions, especially those of metals and PCDD/Fs, which could affect the health of the population living in the area. Previously to regular operations (1996) the baseline levels of PCDD/Fs in soil and vegetation samples collected near the HWI were determined^{2,3}. A second survey was carried out two years later (1998) in order to establish the temporal variation in PCDD/F concentrations in soil and vegetation samples taken at the same sampling points⁴.

Vegetation is considered an adequate short-term environmental monitor for PCDD/Fs⁵. Therefore, in the surveillance program of the facility (1999-2003), herbage samples (40) were annually collected at the same sampling points in which baseline samples had been taken^{6,7}. Moreover, considering soil as a suitable long-term monitor for PCDD/Fs⁸, 40 soil samples in this matrix were again collected in 2001 and 2003 to examine the temporal variations of PCDD/F levels in the area⁹. In the present study, we present the concentrations of PCDD/Fs in soil and vegetation samples collected in the vicinity of the HWI after 5 years of regular operations.

Materials and methods

The HWI operates with a rotator burning furnace at 1100°C. Its capacity is approximately 30,000 tones/year. The emission control systems consist on an electrostatic precipitator, a catalytic converter (selective catalytic reduction, SCR) and a humid scrubber.

Sampling: In April 2003, duplicate soil and herbage samples were collected near the HWI, at the same 40 points in which baseline (1996 and 1998) samples had been taken. From those, 30 were catalogued as rural samples, while the remaining 10 were considered as urban samples. Soil samples corresponded to surface soil (upper 5 cm of column). In the laboratory, they were dried at room temperature until constant weight, and sieved through a 2 mm mesh screen to achieve a homogeneous grain distribution. Herbage samples, which reached 25 cm during the sampling period, were collected by cutting at a height of approximately 4 cm above soil level, and dried at room temperature. All samples were adequately stored until the analytical process.

Analytical procedure: PCDD/F analyses were carried out as previously reported^{3,10}, following an adaptation of the US EPA 1613 method. After shredding, 50 g of sample were taken and several ¹³C internal standards were added. They were treated with hot HCl 1N, filtered and dried at 60°C. Extraction was done on a Soxhlet with toluene for 24 h. Clean-up process based on three consecutive columns (silica with sulfuric acid, multi-step silica and Fluorisil) and a pass through graphite carbon tubs. The extracted was reduced with N₂ and several recover standards were added. PCDD/F determination was done with high-resolution gas chromatography coupled to high-resolution mass spectrometry (HRGC/HRMS) using RTX-5 and DB-Dioxin as chromatographic columns.

Data analysis: Statistical package SPSS 11.0 was used to perform all calculations. When the PCDD/F congener concentration was below the limit of detection, it was assumed that it was one half of the respective limit. For soils, comparisons were done applying the Kruskal-Wallis test taking into account that all samples showed a non-parametric distribution. For herbage, parametric distribution of data allowed to use ANOVA tests to assess significancy of the differences.

Results and discussion

Table 1 summarizes the concentrations of PCDD/Fs in soils and herbage found in the 1998 baseline survey and those of the current investigation. In the 1998 baseline survey, PCDD/F concentrations in soils ranged from 0.12 to 17.20 ng I-TEQ/kg (dry matter), with a median of 0.75 ng I-TEQ/kg (dry matter) and a mean value of 1.59 ng I-TEQ/kg (dry matter). In the current study, PCDD/F concentrations were in the interval from 0.10 to 3.66 ng I-TEQ/kg (dry matter), with median and mean values of 0.56 and 0.77 ng I-TEQ/kg (dry matter), respectively.

Table 1: PCDD/F concentrations (ng I-TEQ/kg dry matter) in soil and herbage samples collected in the vicinity of the HWI in 1998 and 2003 (before and 5 years after regular operations).

	Soil			Herbage		
	1998	2003	Variation (%)	1998	2003	Variation (%)
Urban	2.21	0.84	-62	0.29	0.22	-24
Rural	0.62	0.53	-15	0.22 ^a	0.20 ^b	-9
TOTAL	0.75	0.56	-25	0.24	0.21	-13

Data are given as median values. Different superscripts (a,b) indicates significant differences at $p < 0.05$.

PCDD/F levels diminished in 24 of the 40 soil samples, whereas the remaining 16 showed increases of different consideration. Although a decrease of 25% in the median values was noted, no significant differences were found between 1998 and 2003. In general terms, PCDD/F concentrations decreased close to the HWI (<500 m), increased slightly at distances of 1000-1500 m and diminished at greatest distances (Figure 1).

Urban samples showed higher PCDD/F concentrations than rural ones (median values: 0.84 vs 0.53 ng I-TEQ/kg dry matter). Concentrations in both areas decreased respect to the baseline levels, especially in urban sites, which showed a median concentration of 2.21 ng I-TEQ/kg (dry matter) in 1998.

Most of the tetra- to octa-PCDD/Fs could be detected. In the baseline study, 2,3,7,8-TCDD showed concentrations above the limit of detection in 20 of the 40 samples (detection limit: 0.02 ng I-TEQ/kg dry matter), with a maximum concentration of 0.50 ng I-TEQ/kg (dry matter). In the present survey, 2,3,7,8-TCDD concentrations were only detected in 14 samples, with a maximum of 0.13 ng I-TEQ/kg (dry matter). 2,3,7,8-TCDD mean concentrations were 0.10 and 0.02 ng I-TEQ/kg (dry matter) in 1998 and 2003, respectively. On the other hand,

OCDD ranged from 4.07 to 527 ng I-TEQ/kg (dry matter) in 1998, and from 0.38 to 460 ng I-TEQ/kg (dry matter) in the present study.

With regard to the concentrations of the 17 individual congeners in soils, the highest chlorinated PCDD/Fs mainly accumulated in this matrix. In most samples, OCDD was the predominant congener, followed by 1,2,3,4,6,7,8-HpCDD and OCDF.

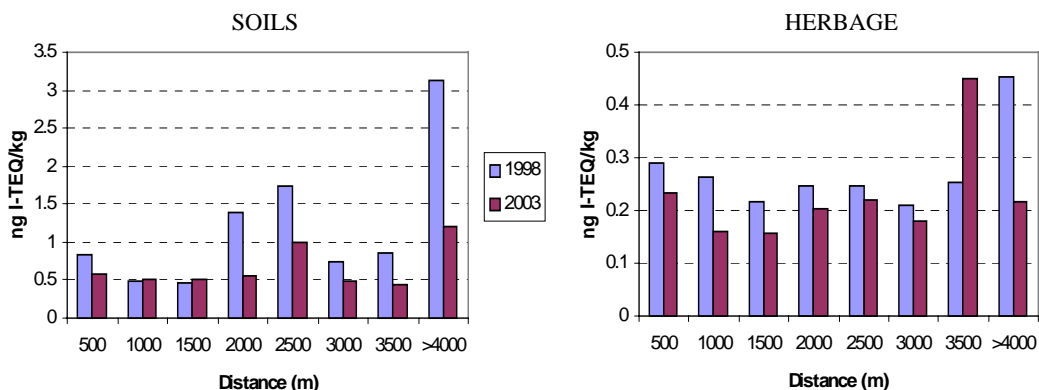


Figure 1: PCDD/F concentrations in soil and herbage samples according to the distances from the HWI. Baseline (1998) and current (2003) data.

In order to assess if the emission sources of PCDD/Fs could have changed in recent years, a Principal Component Analysis (PCA) was applied (Figure 2). PCA showed a two-dimensional model, which would explain 81.7% of the variance. The first component, 54.1% of the variance, is highly correlated with the lowest-chlorinated congeners (tetra- and pentaCDD/F), whereas the second one, which explains the remaining 27.6% of the variance, is correlated with the high-substituted compounds (hepta- and octaCDD). All samples appear basically located in a main cluster in the scatterplot of the components score. The few outlier samples (SV7, SV6, N5 in the first component, and E5 in the second one) correspond to sampling points located far away from the HWI. Consequently, the relatively high concentrations here noted could be probably explained by specific contamination sources not directly related with the facility.

The mean levels observed in soils surrounding the HWI were very similar to those found near the MSWI in 1997 and 1999 (1.17 and 1.20 ng I-TEQ/kg, respectively)⁵. On the other hand, PCDD/F concentrations in soils directly affected by other MSWIs in Catalonia were notably higher: 14.95 ng I-TEQ/kg¹¹ and 5.49 ng I-TEQ/kg¹².

In spite of the current environmental levels of PCDD/Fs in the area under evaluation, which is highly industrialized, the present concentrations in soils are relatively low when compared with those from recent reports. Thus, Cheng et al.¹³ found a mean PCDD/Fs concentration of 3.03 ng I-TEQ/kg in 8 soils collected near Hsinchu's MSWI (Taiwan), while Caserini et al.¹⁴ reported PCDD/F levels between 0.08 and 1.5 ng I-TEQ/kg in soils collected near 3 MSWIs from Italy. On the other hand, average PCDD/F concentrations in soils near the HWI under study are lower than the target concentration marked by the German BLAG (Bund-Länder Arbeitsgruppe) of 5 ng I-TEQ/kg¹⁵.

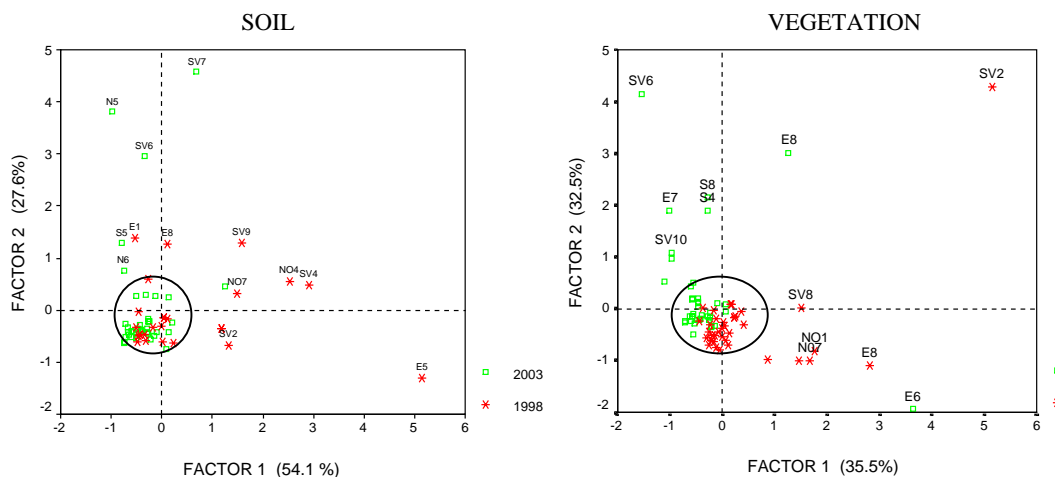


Figure 2: Principal component plot of soil and vegetation samples collected in 1998 and 2003.

In 1998, PCDD/F concentrations in herbage samples ranged from 0.14 to 2.01 ng I-TEQ/kg (dry matter), with median and mean values of 0.24 and 0.31 ng I-TEQ/kg (dry matter), respectively (Table 1). In the present study, PCDD/F concentration ranged between 0.05 and 0.93 ng I-TEQ/kg (dry matter) (median value of 0.21 ng I-TEQ/kg dry matter and mean value of 0.22 ng I-TEQ/kg dry matter). Urban median concentrations seems to be slightly higher than those belonging to rural samples (0.22 vs 0.20 ng I-TEQ/kg (dry matter). However, as in the case of soils, there was a decrease with respect to the 1998 baseline study (0.29 and 0.22 ng I-TEQ/kg (dry matter), respectively).

PCDD/F concentrations decreased in 28 of the 40 samples, while the remaining 12 samples showed an increase of different nature, depending mainly of the proximity to possible local pollution sources. The PCDD/F concentrations profile according to the distance from the HWI is depicted in Figure 1. Only in samples

collected at 3500 m from the plant, PCDD/F levels in vegetation increased. A global reduction of 13% in the median value was noted. Anyway, ANOVA test did not show significant differences in the PCDD/F levels in herbage before and after 5 years of regular operations in the facility.

Most PCDD/F congeners could be detected in all herbage samples. In 1998, 2,3,7,8-TCDD presented a maximum concentration of 0.21 ng I-TEQ/kg (dry matter) and a median of 0.02 ng I-TEQ/kg (dry matter). Moreover, in the present survey maximum and median levels decreased to 0.07 and 0.01 ng I-TEQ/kg (dry matter), respectively, being this congener detected only in 15 of the 40 samples.

PCDD/F congener profile of vegetation samples was very similar to that found in soils. Thus, the highest-substituted compounds were the most concentrated in vegetation, with special attention to OCDD, which showed mean values of 3.93 and 1.78 ng I-TEQ/kg (dry matter) in 1998 and 2003, respectively. PCA allowed representing a two-dimensional model which would explain 67.8% of the variance (Figure 2). The first component (35.5% of the variance) was correlated with all PCDD congeners, as well as with TCDF, while the second component, which would explain the remaining 32.3%, was more correlated with HxCDFs and HpCDFs. Most herbage samples collected in both studies are grouped into a sole main cluster, which means that emission sources of PCDD/Fs did not change in the last 5 years. A few samples collected in 1998 seemed to show an increase in Factor 1, while some herbage samples collected in the present survey showed a higher concentration of Factor 2. The fact that these samples are located far away from the HWI, together with the finding that those collected at the same wind direction did not show any variation, suggest that these sampling points have been exposed to local pollution sources not directly related with the emissions of PCDD/Fs from the HWI.

PCDD/F levels in vegetation were similar to those found in the vicinity of the MSWI, where mean concentrations of 0.23 and 0.11 ng I-TEQ/kg were found in 1997 and 1999, respectively⁵. Previous investigations in the neighborhood of other MSWIs of Catalonia showed PCDD/F levels in herbage samples of 0.66 and 0.77 ng I-TEQ/kg^{12,16}. On the other hand, Martínez et al.¹⁷ compared PCDD/F concentrations in burned and unburned material after forest fires in Catalonia, finding values ranging 0.45 to 0.65 ng I-TEQ/kg in several samples of unburned vegetation.

The absence of significant increases in the concentrations of PCDD/Fs in soil and herbage samples collected in the surroundings of the HWI in 1998 and 2003, clearly indicates that, to date, comparatively this facility is not being an important source of environmental PCDD/Fs in the area.

Acknowledgements

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