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

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Introduction

The construction in Constanti (Catalonia, Spain) of a new hazardous waste incinerator (HWI) was finished in 1999. Because this is the first HWI in Spain, the concern about its environmental impact and health risks is notable. Aliphatic hydrocarbons, esters, ketones, chlorobenzenes, chlorophenols, nitroaromatic compounds and polycyclic aromatic hydrocarbons (PAHs) have been reported to be the main compounds detected in the flue gas of HWIs[1]. Although polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) are not included among these contaminants, PCDD/Fs can be also emitted at detectable levels[2]. Because of the public fear about PCDD/Fs, the knowledge of the health risks derived from emissions of these compounds byHWIs is a matter of concern.

The atmospheric concentrations of PCDD/Fs vary according to a number of factors such as the prevailing meteorological conditions. Moreover, the environmental fate and impact of PCDD/Fs are different from season to season. Therefore, the atmospheric levels of PCDD/Fs are not necessarily the best monitor for these organic pollutants. Because PCDD/F emissions from incinerators result in subsequent deposition onto soil and vegetation, in a pre-operational monitoring program (1996) the levels of PCDD/Fs were determined in soil and herbage samples collected in the vicinity of the HWI[3,4]. To have a knowledge about the temporal variation of the environmental PCDD/F levels in the area under potential influence of the new HWI previous to the operation of the plant, in 1998 a second series of soil and vegetation samples was again collected for PCDD/F analyses. This paper presents the concentrations of PCDD/Fs in vegetation and the comparison with those found in the 1996 survey. A companion paper shows the results in soil samples[5].

Methods and Materials

In April 1998, two years after the first sampling, 40 herbage samples were collected in the same points in which samples had been taken in the 1996 survey[4]. Duplicate herbage samples were obtained by cutting at a height of approximately 4 cm above soil level. They were dried at room temperature and stored until analysis. About 50 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 reported[4]. 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 and on a DB-Dioxin (60 m x 0.25 mm x 0.25μm) capillary column. The latter was used to separate those 2,3,7,8-congeners that were not resolved on the SPB-5 column. Monitored masses were those proposed by EPA 1613 method.

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

Table 1 shows the individual concentrations of PCDD/Fs for the 40 herbage samples collected in 1998 in rural and urban areas in the vicinity of the new HWI. PCDD/F levels obtained in the 1996 survey[4], as well as the percentage of temporal variation of the I-TEQ values are also shown for each sample. In the present study, PCDD/F concentrations ranged from 0.14 to 2.01 ng I-TEQ/kg (dry matter) (median and mean values: 0.23 and 0.31 ng I-TEQ/kg, respectively), while in the 1996 survey PCDD/F concentrations ranged from 0.24 to 1.22 ng I-TEQ/kg (dry matter) (median and mean values: 0.53 and 0.61 ng I-TEQ/kg, respectively). An individual comparison of the results shows that PCDD/F levels decreased in 35 of the 40 samples. By contrast, 4 samples showed increases in the concentrations of PCDD/Fs, while no changes were noted in one sample. The average temporal variation of the PCDD/F levels (I-TEQ values) in vegetation samples during the period 1996-1998 consisted in a significant decrease: 56% ($p < 0.001$).

Table 1. PCDD/F concentrations (ng I-TEQ/kg dry matter) in vegetation samples collected in the vicinity of a new hazardous waste incinerator before operation (1996 and 1998). Temporal variation

		Herbage					Herbage		
Sample	Area	1996	1998	Variation (%)	Sample	Area	1996	1998	Variation (%)
E-1	R	0.50	0.21	-58.0	NO-5	R	0.34	0.32	-5.9
E-2	R	0.50	0.32	-38.5	NO-6	R	0.36	0.21	-41.7
E-3	R	0.24	0.19	-20.8	NO-7	R	0.42	0.48	14.3
E-4	R	0.25	0.22	-12.0	S-1	R	0.28	0.18	-35.7
E-5	R	0.65	0.18	-72.3	S-2	R	1.05	0.34	-67.6
E-6	R	0.52	0.17	-67.3	S-3	R	0.49	0.23	-53.1
E-7	R	0.37	0.14	-62.2	S-4	R	0.60	0.17	-71.7
E-8	U	0.83	0.51	-38.6	S-5	R	0.77	0.19	-75.3
E-9	R	0.33	0.43	30.3	S-6	R	0.72	0.19	-73.6
N-1	R	0.77	0.25	-67.5	S-7	R	0.68	0.21	-69.1
N-2	R	0.51	0.19	-62.7	S-8	R	0.32	0.32	0.0
N-3	R	0.53	0.24	-54.7	SV1	U	1.08	0.18	-83.3
N-4	R	1.14	0.28	-75.4	SV2	U	0.82	2.01	145.1
N-5	R	0.88	0.30	-65.9	SV4	U	0.57	0.17	-70.2
N-6	R	0.53	0.27	-49.1	SV6	U	0.71	0.24	-66.2
N-7	R	0.56	0.19	-66.1	SV7	U	1.22	0.21	-82.8
NO-1	R	0.44	0.52	18.2	SV8	U	0.97	0.45	-53.6
NO-2	R	0.39	0.20	-48.7	SV9	U	0.87	0.32	-63.2
NO-3	R	0.35	0.21	-40.0	SV10	U	0.54	0.36	-33.3
NO-4	R	0.39	0.32	-17.9	SV11	U	0.96	0.25	-74.0

R= rural area; U= urban area

Higher PCDD/F levels were found in the herbage samples collected in the urban than in the rural area. PCDD/F median values in 1996 were 0.83 and 0.50 ng I-TEQ/kg (dry weight) for urban and rural samples respectively, while in the present study median values were 0.29 and 0.22ng I-TEQ/kg (dry weighy) for urban and rural samples, respectively. In both studies the differences reached the level of statistical significance ($p < 0.05$). In turn, the PCDD/F congener profiles for samples collected during 1996 and again in 1998 are depicted in Figure 1. 2,3,7,8-TCDD was the congener showing a higher contribution to the total I-TEQ.

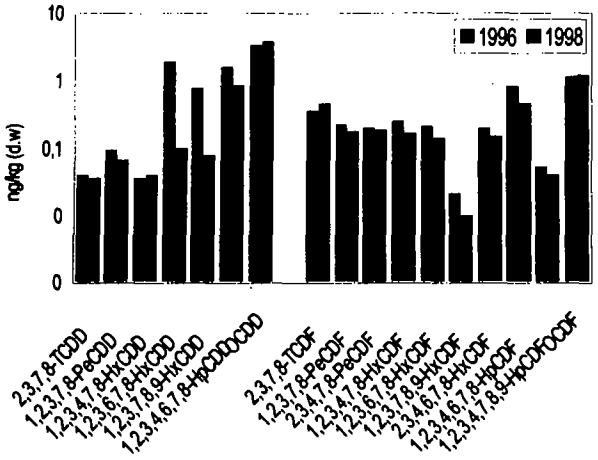

Figure 1. PCDD/F congener profiles in vegetation samples collected in 1996 and 1998 in the vicinity of a new HWI.

PCDD/F congeners found in environmental samples show a composition which is characteristic of their sources and their subsequent environmentally-included decomposition reactions. To assess if PCDD/F emission sources in the area under study changed during the period 1996-1998, a multivariate analysis (PCA) of the data was applied. The scatterplot of the component scores on both principal components (PC) is presented in Figure 2. Two main clusters were clearly identified (1996 and 1998 surveys), which means that a modification of the PCDD/F emission sources occurred during this period. On the other hand, when a multivariate analysis of the results corresponding to the 80 (40 + 40) herbage samples collected in 1996 and 1998 in urban and rural areas in the vicinity of the new HWI was done, two clusters were also identified (Figure 3). One of these clusters showed a big dispersion, which suggests that vegetation can be more affected by punctual PCDD/F sources than soils[5].

PCDD/Fs are introduced in the atmosphere by various sources forming an uniform ambient air. During transport, wet and dry deposition, as well as due to chemical transformation and degradation processes, the composition of the PCDD/F mixture can be altered. Although the atmosphere is the primary medium of discharge, it is essential to quantify the presence of PCDD/Fs in other media taking into account that they can be the main sources for human exposure. For example, the air-vegetation-livestock-human pathway is probably the most important route of human exposure. In relation to this, vegetation is a suitable monitor to give information on the short-term exposure to PCDD/Fs. As in the present survey, recent studies also found significant decreases in the levels of PCDD/Fs in vegetation[6-9]. The results of the current study will be useful to establish the environmental impact of the new HWI, but can be also of interest for further studies on PCDD/F levels in vegetation.

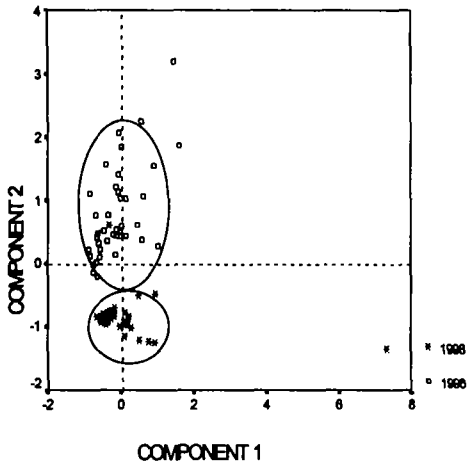

Figure 2. Principal component plot of vegetation samples collected in 1996 (n=40) and 1998 (n=40).

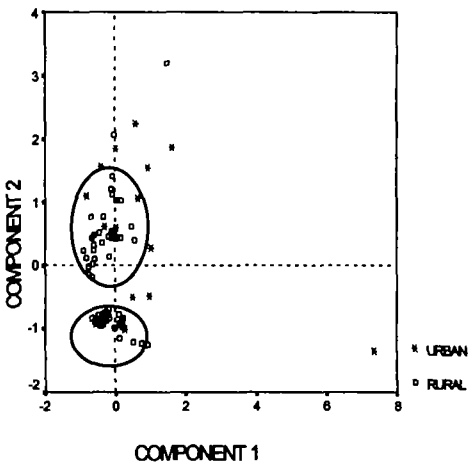

Figure 3. Principal component plot of vegetation samples collected in urban (n=20) and rural (n=60) areas.

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