LEVELS OF PCDD/Fs IN SAMPLES OF HERBAGE AND AMBIENT AIR IN THE VICINITY OF A MUNICIPAL SOLID WASTE INCINERATOR

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Introduction

In 1991, a municipal solid waste incinerator (MSWI) placed in Tarragona (Catalonia, Spain) started regular operations. Between 1996 and 1999, the environmental impact of the facility regarding to polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) emissions was assessed[1]. The advantages of installing a new gas cleaning system were also established[2]. In 2002-2005, a new campaign of the surveillance program was carried out by analyzing the levels of PCDD/Fs in soil and/or herbage samples collected in the vicinity of the MSWI[3]. The results showed that, in principle, the influence on the plant was not relevant in comparison with other potential sources of PCDD/Fs within the area. However, the presence of some confounding factors increased the difficulty of assessing the risks derived of the PCDD/F emissions from the MSWI. In 2007, a 3rd campaign was initiated by measuring the concentrations of PCDD/Fs in herbage samples collected in the surroundings, and by establishing the temporal trend in relation to the baseline survey (1999) and the previous survey (2004). Furthermore, PCDD/F levels in air were also determined at the same sampling sites. The results of the initial study of this last survey are here presented.

Materials and methods

The MSWI of Tarragona is located in an industrial area with other potentially important pollutant sources, and relatively close to the village of Constantí and the city of Tarragona. It has an annual incineration capacity of approximately 154,000 ton/year. In June 2007, herbage and air samples were collected in 8 sampling points at different distances (250, 500, 750, 1000, 1250, and 1500 m) and directions (NE, NW, SE and SW) from the MSWI. These sites were chosen taking into account the predominant wind directions in the area, as well as other parameters, to minimize the influence of other potential pollutant sources in the same zone. Herbage (*Piptatherum paradoxum* L.) samples were collected by cutting the plants at 5 cm above ground. They were kept in double aluminum foils and, once in the laboratory, dried at room temperature until analyses. Air samples were collected using a high volume active sampler TE-1000 (Tisch Environmental, Cleves, OH, USA). The airflow was calibrated to 0.225 m^3/min and the sampling duration was approximately 48 h.

Herbage samples were analyzed following the US EPA method 1613, whereas air samples were analyzed according to the German VDI 3499 method. $^{13}C_{12}$-isotopic recovery internal standards were added to the samples. Subsequently, an ASE (Accelerated Solvent Extraction) was done with a Dionex 300 by using toluene as solvent. The extract was then subjected to an acid/base clean-up procedure followed on micro columns of silica gel and alumina. The concentrations of PCDD/Fs were determined by high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). Recovery percentages ranged from 56 to 82%, and from 60 to 130% in herbage and air samples, respectively. Results were not recovery corrected according to these values.

For calculations, when a value was under its detection limit (LOD), the concentration was assumed to be half of that LOD (ND = 1/2 LOD). Statistical significance was determined by analysis of variance (ANOVA) or a Kruskal-Wallis test, depending on whether or not data followed a normal distribution. A probability of 0.05 ($p<0.05$) was considered as significant. The statistical software SPSS version 15.0 was used for data analysis. Toxic equivalents (TEQ) were calculated according to the 2005 WHO-TEFs[4].

Results and discussion

PCDD/Fs in herbage

The individual PCDD/F concentrations in the 8 herbage samples collected around the MSWI in 2007, as well as the temporal trend with respect to the 1999 and 2004 surveys, are shown in Table 1. In the present study, PCDD/F levels ranged from 0.05 to 0.16 ng WHO-TEQ/kg (d.w.), with median and mean values of 0.09 ng WHO-TEQ/kg (d.w.) (both values). These concentrations are in the low range when comparing with those found in other industrial, residential/urban or even background areas of Catalonia[5, 6].

The current PCDD/F concentrations decreased significantly ($p<0.05$) in comparison with those of the last survey (2004), while they were similar to the 1999 levels. Between 1999 and 2007, PCDD/F concentrations decreased in 2 of the 8 sampling sites, were maintained in 2, and increased in the remaining 4. On the other hand, PCDD/F levels decreased in 6 sites, while they increased in the other 2. In 2007, the highest concentration was found at the south east direction (250 m) (0.16 ng WHO-TEQ/kg d.w.), while the lowest concentration (0.05 ng WHO-TEQ/kg d.w.) was observed at the south west (1250 m).

The 2007 PCDD/F congener profile in vegetation samples is depicted in Figure 1 together with the profiles corresponding to immission and emission levels of PCDD/Fs. At first glance, no important differences between the three profiles was observed, being OCCD followed by 1,2,3,4,6,7,8-HpCDD the most abundant congeners.

PCDD/F concentrations in herbage samples are a good indicator of short-term environmental emissions. Herbage receives PCDD/Fs from air through wet and dry particle deposition and gaseous diffusion, as well as the adherence of resuspended particles from soil[7]. Once emitted, the PCDD/F behavior is highly influenced by the meteorological conditions. Therefore, the small variations noted probably might be caused by the different rain pattern during the months previous to the sampling, the wind force, or the solar radiation. Moreover, environmental PCDD/F levels are more and more conditioned by diffuse sources such as traffic vehicles, uncontrolled fires, or domestic heating among others[8].

Figure 2 shows the PCDD/F concentrations in herbage according to the different sampled distances and directions from the MSWI. As in 2004, no important differences were observed. However, the sample collected at the nearest site from the facility (250 m) showed the highest concentration. These relatively higher levels near the MSWI could be due to the wet deposition and the leak of the ashes during their handling, transport and storage. However, the most plausible reason is the intense heavy traffic in this site, which is situated next by a roundabout in the main access to the industrial complex.

With respect to the 1999 survey, a decrease in the concentrations at 250 m (24%) was observed the south west (1250 m) showed, while PCDD/F levels increased at 500 m (50%), 1250 m (75%), and 1500 m (71%). On the other hand, in comparison with 2004, PCDD/F concentrations decreased at 500 m (31%), 750 m (60%), 1000 m (48%) and 1250 m (53%). Statistical analysis of data was not possible because in the current study (2007), distances and directions (with the exception of 1000 m and SW) were represented by only 1 site ($n<3$).

A Principal Component Analysis (PCA) was performed in order to study similarities among the sample profiles and hence their sources (Figure 3). PCA (Figure 3) showed almost all samples (SE1 included) clustered together. This is in agreement with the possibility that traffic is the predominant source of PCDD/Fs. A single cluster involves similar PCDD/F sources for near and far samples. Samples SE4 and SW4 collected in 1999 and 2004, respectively, exhibited higher values for component 1, highly correlated with penta- and hexa- furans, while NE3 collected in 2004, showed higher values for component 2 correlated with 1,2,3,4,7,8-HxCDD and 1,2,3,6,7,8-HxCDD. These samples were probably affected by different sources of PCDD/Fs such us accidental fires, agricultural burning or industrial activities among others.

PCDD/Fs in air samples

The individual concentrations of PCDD/Fs in ambient air sampled near the MSWI are summarized in Table 1. Total PCDD/F concentrations ranged from 5.1 to 32.5 fg WHO-TEQ/m^3 (in SW4 and SE1, respectively), with a

mean value of 12.0 fg WHO-TEQ/m^3. Low-chlorinated dioxins and high-chlorinated furans (1,2,3,7,8,9-HxCDF, 1,2,3,4,7,8,9-HpCDF and OCDF) were often under its respective LOD. OCDD was the most abundant congener, while 2,3,4,7,8-PeCDF was the main contributor to total WHO-TEQ/m^3. The concentrations found in the present study are in the low range of those reported in other industrial areas of Catalonia[9].

With respect to the different distances and directions, the highest PCDD/F air concentrations were found at 250 m and SE, respectively (Figure 4). As in herbage, the highest levels in the nearest site to the MSWI might be due to the heavy traffic, as it was seen in the previous PCA.

In summary, the results of the current survey (2007), together with those obtained in our previous studies, show that the MSWI does not have a remarkable environmental impact in comparison with other PCDD/F sources. PCDD/F levels in herbage and air samples were similar to those found in other industrial, urban or even background areas. However, to identify the real traffic contribution on total PCDD/F levels, it would be highly desirable to carry out a specific study on SE1, where higher levels were detected in both air and herbage.

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Table 1: PCDD/F concentrations in herbage and air samples collected around the MSWI

		Herbage					Air
		YEAR			% of variation		YEAR
Sample	Distance (m)	1999	2004	2007	99-07	04-07	2007
SE1	250	0.21	0.15	0.16	-24	7	32.5
SW2	500	0.06	0.13	0.09	50	-31	5.5
NE3	750	0.10	0.25	0.10	0	-60	8.5
NW4	1000	0.07	0.10	0.08	14	-20	12.3
SE4	1000	0.08	0.11	0.06	-25	-45	19.9
SW4	1000	0.05	0.23	0.05	0	-78	5.1
SW5	1250	0.04	0.15	0.07	75	-53	8.5
NW6	1500	0.07	0.09	0.12	71	33	3.9
Total TEQ		0.085^a	0.151^b	0.091^a	7	-40	12.0

For 1999 and 2004 data, PCDD/F concentrations in herbage are given in ng I-TEQ/kg (d.w.), while those of 2007 are in ng WHO-TEQ/kg (d.w.). Levels of PCDD/Fs in ambient air are presented in fg WHO-TEQ/m^3.
[a,b] Different superscripts indicate significant differences between years ($p<0.05$).

Figure 1: PCDD/F congener profiles of herbage, air (immission) and emissions of the MSWI

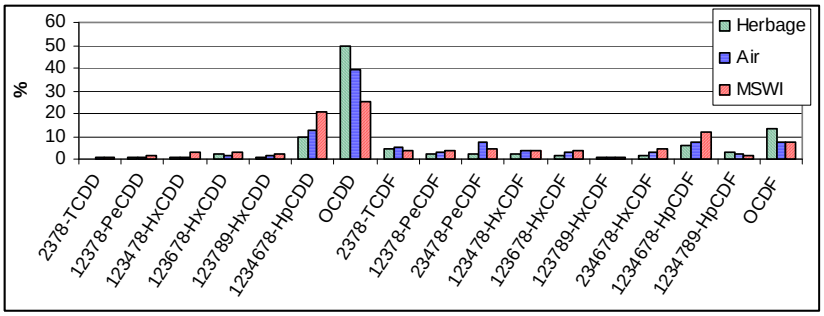

Figure 2: PCDD/F concentrations in herbage according to different distances (meters) and direction to the MSWI

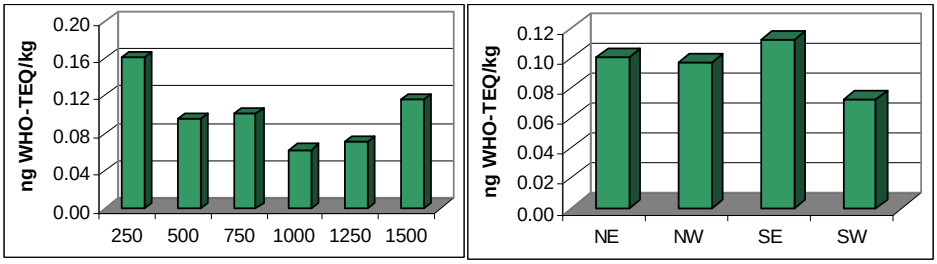

Figure 3: PCA of the herbage samples collected around the MSWI in 1999, 2004 and 2007

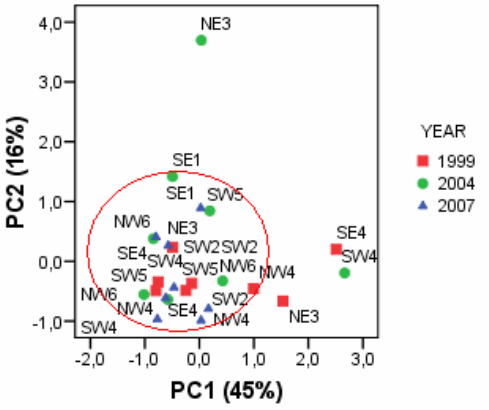

Figure 4: PCDD/F concentrations in ambient air according to the distance (meters) and direction to the MSWI