MONITORING PCDD/F CONCENTRATIONS IN HERBAGE SAMPLES NEAR A MUNICIPAL WASTE INCINERATOR

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Introduction

The emission products of municipal solid waste incinerators (MSWI), polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) have generated a great public concern. Because of their notable toxic properties, PCDD/Fs have received prolonged attention by the scientific community and by environmental regulations^{1,2}. While the atmospheric concentrations of PCDD/Fs vary according to a number of factors such as the prevailing meteorological conditions, the environmental fate and impact of PCDD/Fs are also different from season to season. Taking into account that atmospheric deposition is the main mean of supplying PCDD/Fs to soil and vegetation^{3,4} and that they can be the main sources for human exposure, these matrices have been used as an environmental monitor of PCDD/Fs in the vicinity of MSWI⁵⁻⁷.

Since 1975, a MSWI is operating in Montcada (Barcelona, Spain). Until recently, an electrostatic precipitator was used as emission control device. In March 1999, a modernisation of the flue gas cleaning system was carried out. An acid gas (HCl/SO₂) and metal emission limit equipment was installed and an active-carbon adsorption filter was added to the fabric filter. Consequently, PCDD/F emissions have been reduced from average values higher than 10 ng I-TEQ/Nm³ to levels under the legal limit of 0.1 ng I-TEQ/Nm³.

Before and after introduction of the technical improvements in the facility, herbage samples were collected near the plant and PCDD/F levels determined⁸⁻¹⁰. This paper presents these levels, as well as a comparison of the concentrations of PCDD/Fs in vegetation in the periods 1996-1997, 1997-1998, 1998-2000 and 2000-2001.

Methods and Materials

In October 2001, 12 herbage samples were collected in the vicinity of the MSWI. Parameters such as main wind directions (NE, NO, S) in the area under potential influence of the facility, distances from the MSWI to the sampling points (100, 200, 500 and 1500 m), as well as the specific places in which samples had been previously taken (period 1996-2000)⁸⁻¹⁰ were again the same.

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 reported⁶. 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 and on a DB-Dioxin (60 m x 0.25 mm x 0.25 mm)

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). The non parametric Kruskal-Wallis test and a multivariate analysis of the results was done. All calculations were performed using the SPSS-10.0 statistical software.

Results and Discussion

Table 1 summarizes the individual concentrations of PCDD/Fs for the 12 herbage samples collected during the years 1996, 1997, 1998, 2000 and 2001 in the vicinity of the MSWI, as well as the percentage of temporal variation of the I-TEQ values. In the period 1996-1998 (before the modernisation of the flue gas cleaning system), PCDD/F concentrations ranged from 0.73 to 2.92 ng I-TEQ/kg (dry matter) with median values of 1.88 (1996), 1.27 (1997) and 0.79 (1998) ng I-TEQ/kg (dry matter). In the 2000 survey, when the active-carbon adsorption filter was added to the fabric filter, PCDD/F concentrations ranged from 0.43 to 1.12 ng I-TEQ/kg (dry matter), with a median value of 0.70 ng I-TEQ/kg. In the present study, PCDD/F concentrations ranged from 0.13 to 0.54 ng I-TEQ/kg (dry matter) with a median value of 0.29 ng I-TEQ/kg. Although between 1996 and 1998 there was a progressive decrease in the PCDD/Fs levels, the most important reduction was observed in the period 2000-2001: 59% (p < 0.05). PCDD/F levels decreased year after year (Figure 1) until reaching a global reduction of 85%, when the entire period 1996-2001 was considered.

Table 1. PCDD/F concentrations (ng I-TEQ/kg dry matter) in herbage samples collected in the vicinity of a municipal waste incinerator in 1996, 1997, 1998, 2000 and 2001: Temporal variation.

	Herbage					Variation (%)			
Sample	1996	1997	1998	2000	2001	1996-1997	1997-1998	1998-2000	2000-2001
NE1	1.95	1.19	1.94	1.12	0.36	-39	63	-42	-68
NO1	2.11	1.78		1.10	0.41	-16			-63
S1	2.92		1.04	0.90	0.18			-14	-80
NE2	1.61	0.92	0.73	0.70	0.29	-43	-21	-4	-59
NO2	2.15	1.60	1.00	0.48	0.32	-26	-38	-52	-33
S2	2.38	1.90	0.94	0.66	0.17	-20	-51	-29	-74
NE3	1.93	1.42	0.78	0.98	0.20	-26	-45	26	-80
NO3	2.30	0.96	0.96	0.51	0.13	-58	0	-47	-75
S3	1.68	1.57	1.47	0.43	0.27	-7	-6	-71	-37
NE6	1.27	1.02	0.50	1.66	0.54	-20	-51	232	-67
NO6	1.94	0.75	1.07	0.72	0.33	-61	43	-33	-54
S6	2.59	1.95	0.77	0.64	0.29	-25	-61	-17	-55
I-TEQ*	1.88	1.27	0.79	0.70	0.29	-32 ²	-38 1	-11	-59 ²

 $^{^{1}}$ p<0.01, 2 p<0.001

^{*}Median values

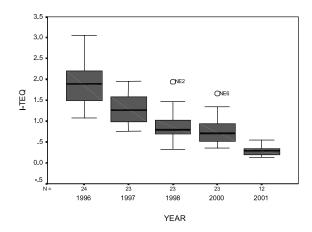


Figure 1. Box diagram of PCDD/Fs (ng I-TEQ/kg dry matter) in herbage samples collected in 1996, 1997, 1998, 2000 and 2001 in the vicinity of a MSWI.

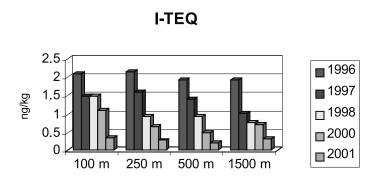


Figure 2. PCDD/F levels in herbage samples collected at different distances from a MSWI in 1996, 1997, 1998, 2000 and 2001.

As in the present survey, other recent studies also reported significant decreases in the levels of PCDD/Fs in vegetation¹¹⁻¹³.

In Figure 2, it can be clearly seen that PCDD/F concentrations diminished progressively in the samples collected at concentric distances from the plant (100, 250, 500 and 1500 m).

In summary, the current results obtained two years after the active-carbon adsorption filter was added to the plant, show a remarkable decrease of PCDD/F levels in herbage samples collected near the MSWI. Data about PCDD/F emissions and PCDD/F deposition in soils, which are currently being analyzed should complete the evaluation of the environmental impact of the MSWI on the area under its direct influence.

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