# PCDD/PCDF IN THE VICINITY OF A HAZARDOUS WASTE INCINERATOR IN CATALONIA, SPAIN. II. LEVELS IN HERBAGE

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## INTRODUCTION

In 1999, the construction in Constantí (Catalonia, Spain) of a new hazardous incinerator (HWI) was finished. Since this was the first and up till now the only HWI in Spain, the concern about its potential environmental impact and health risks was notable taking into account that until recently, waste incinerators were among the major contributors to the environmental concentrations of PCDD/Fs.[1,2]

The atmospheric concentrations of PCDD/Fs can vary according to factors such as the prevailing meteorological conditions, while the environmental fate and impact of these organic pollutants are different from season to season. Consequently, in order to evaluate the environmental impact of a facility emitting PCDD/Fs, their atmospheric levels are not necessarily the most adequate monitor for these compounds. Atmospheric deposition is the main mean of supplying PCDD/Fs to soils and vegetation[3,4] . Since these environmental matrices can be the main sources for human exposure, they were used in a pre-operational monitoring program of PCDD/Fs, which was initiated during the construction of the facility[5,6]. In relation to vegetation, it is a suitable monitor to give information on the short-term exposure to PCDD/Fs. To have a complete knowledge about the evolution of the environmental PCDD/F levels in the area under potential influence of the new HWI, two baseline studies were carried out in 1996 and 1998[7,8]. Herbage samples were again collected for PCDD/F analyses in 2000 and 2001. The concentrations of PCDD/Fs in these samples for the periods 1998-2000[8] and 2000-2001 are presented in this paper. A companion paper shows the results in soil samples[9].

### Methods and Materials

In April 2001, five years after the first baseline survey, 40 herbage samples were collected in the same points in which samples had been previously taken (1996, 1998 and 2000 surveys). 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[6]. 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.

# LEVELS IN BIOTIC COMPARTMENTS

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-10.0 statistical software.

**Results and Discussion**

Table 1 shows the individual concentrations of PCDD/Fs for the 40 herbage samples collected during the years 1998, 2000 and 2001 in rural and urban areas in the vicinity of the new HWI. The percentages of temporal variation of the I-TEQ values are also given. In the present study, PCDD/F concentrations ranged from 0.12 to 0.85 ng I-TEQ/kg dry matter (median and mean values: 0.19 and 0.21 ng I-TEQ/kg, respectively). In the 2000 study, one year after the plant began regular operations, PCDD/F concentrations ranged from 0.13 to 0.65 ng I-TEQ/kg dry matter (median and mean values: 0.29 and 0.32 ng I-TEQ/kg, respectively). In the 1998 survey (baseline), 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).

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

| | | Herbage | | | Variation (%) | | | | Herbage | | | Variation (%) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | Area | 1998 | 2000 | 2001 | 1998-2000 | 2000-2001 | Sample | Area | 1998 | 2000 | 2001 | 1998-2000 | 2000-2001 |
| E-1 | R | 0.21 | 0.54 | 0.21 | 157.1 | -61.1 | NO-5 | R | 0.32 | 0.36 | 0.22 | 12.5 | -38.9 |
| E-2 | R | 0.32 | 0.38 | 0.20 | 18.8 | -47.4 | NO-6 | R | 0.21 | 0.28 | 0.22 | 33.3 | -21.4 |
| E-3 | R | 0.19 | 0.13 | 0.20 | -31.6 | -53.8 | NO-7 | R | 0.48 | 0.50 | 0.16 | 4.2 | -68.0 |
| E-4 | R | 0.22 | 0.22 | 0.37 | 0.0 | 68.2 | S-1 | R | 0.18 | 0.32 | 0.27 | 77.8 | -15.6 |
| E-5 | R | 0.18 | 0.24 | 0.22 | 33.3 | -8.3 | S-2 | R | 0.34 | 0.30 | 0.18 | -11.8 | -40.0 |
| E-6 | R | 0.17 | 0.33 | 0.16 | 94.1 | -51.5 | S-3 | R | 0.23 | 0.24 | 0.31 | 4.3 | 29.2 |
| E-7 | R | 0.14 | 0.20 | 0.25 | 42.9 | 25.0 | S-4 | R | 0.17 | 0.28 | 0.17 | 64.7 | -39.3 |
| E-8 | U | 0.51 | 0.23 | 0.19 | -54.9 | -17.4 | S-5 | R | 0.19 | 0.47 | 0.22 | 147.4 | -53.2 |
| E-9 | R | 0.43 | 0.34 | 0.17 | -20.9 | -58.8 | S-6 | R | 0.19 | 0.45 | 0.17 | 136.8 | -62.2 |
| N-1 | R | 0.25 | 0.25 | 0.16 | 0.0 | -36.0 | S-7 | R | 0.21 | 0.65 | 0.13 | 209.5 | -80.0 |
| N-2 | R | 0.19 | 0.24 | 0.14 | 26.3 | -43.3 | S-8 | R | 0.32 | 0.39 | 0.18 | 21.9 | -53.8 |
| N-3 | R | 0.24 | 0.43 | 0.17 | 79.2 | -60.5 | SV1 | U | 0.18 | 0.22 | 0.85 | 22.2 | 286.4 |
| N-4 | R | 0.28 | 0.25 | 0.12 | -10.7 | -52.0 | SV2 | U | 2.01 | 0.33 | 0.25 | -83.6 | -24.2 |
| N-5 | R | 0.30 | 0.17 | 0.21 | -43.3 | 23.5 | SV4 | U | 0.17 | 0.33 | 0.16 | 94.1 | -51.5 |
| N-6 | R | 0.27 | 0.22 | 0.15 | -18.5 | -31.8 | SV6 | U | 0.24 | 0.49 | 0.26 | 104.2 | -46.9 |
| N-7 | R | 0.19 | 0.28 | 0.16 | 47.4 | -42.8 | SV7 | U | 0.21 | 0.26 | 0.16 | 23.8 | -38.5 |
| NO-1 | R | 0.52 | 0.32 | 0.17 | -38.5 | -46.9 | SV8 | U | 0.45 | 0.20 | 0.26 | -55.6 | 30.0 |
| NO-2 | R | 0.20 | 0.28 | 0.20 | 40.0 | -28.6 | SV9 | U | 0.32 | 0.35 | 0.25 | 9.4 | -28.6 |
| NO-3 | R | 0.21 | 0.24 | 0.15 | 14.3 | -37.5 | SV10 | U | 0.36 | 0.36 | 0.16 | 0.0 | -55.5 |
| NO-4 | R | 0.32 | 0.34 | 0.12 | 6.3 | -64.7 | SV11 | U | 0.25 | 0.25 | 0.21 | 0.0 | -16.0 |

R= rural area; U= urban area

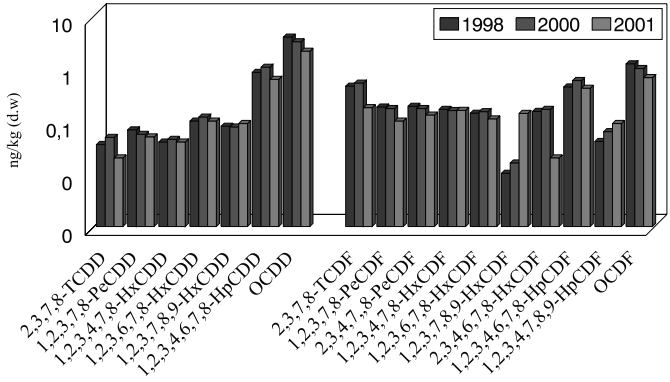


**Figure 1.** PCDD/F congener profile in vegetation samples collected in 1998, 2000 and 2001 in the vicinity of a new HWI.

An individual comparison of the results shows that PCDD/F levels decreased in 34 of the 40 samples and increased in the remaining 6 samples. In the period 1998-2000, an insignificant 3% increase ($p > 0.05$) in the average temporal variation of the PCDD/F levels (I-TEQ values) was observed. In contrast, during the period 2000-2001 a significant decrease of 34% ($p<0.05$) could be noted. These results suggest that PCDD/Fs emissions from the HWI are not the only responsible for the levels of PCDD/Fs in the area under direct influence of the plant. As in the present survey, other recent studies also reported significant decreases in the levels of PCDD/Fs in vegetation[10-12].

In general terms, higher PCDD/F levels were found in herbage samples collected in the urban than in the rural area. PCDD/F median values in 1998 were 0.29 and 0.22 ng I-TEQ/kg dry weight for urban and rural samples, respectively, with the difference being statistically significant ($p<0.05$). In the 2000 survey, the results between urban and rural samples were similar, without differing significantly. In the present study, the median PCDD/F values were 0.23 and 0.18 ng I-TEQ/kg dry weight for urban and rural samples, respectively. The PCDD/F congener profile for herbage samples collected in 1998, 2000 and 2001 is depicted in Figure 1.

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 between the periods 1998-2000 and 2000-2001, 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. Only one main cluster could be clearly identified (1998, 2000 and 2001 surveys). It means that the PCDD/F emission sources during these periods are similar. A multivariate analysis of the PCDD/F levels corresponding to the 40 herbage samples collected in 2001 in urban and rural areas in the vicinity of the HWI was also done (Figure 3). The results of the current study, as well as those from our companion paper[9] show that during the three years of regular operations of the plant, a negative environmental influence on the levels of PCDD/F in herbage samples collected the vicinity of the facility was not noted.

**Acknowledgements**

This research was supported by the Junta de Residus, Department of Environment, Generalitat de Catalunya, Spain.

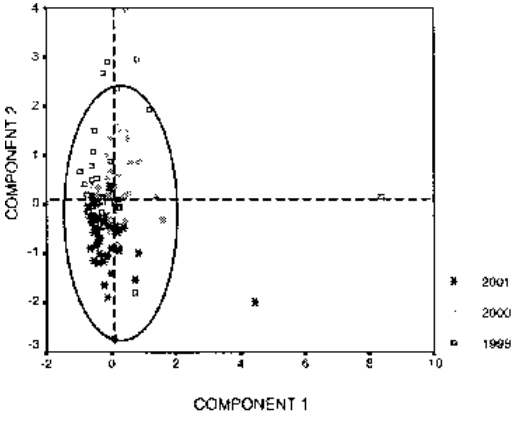


**Figure 2.** Principal component plot of vegetation samples collected in 1998 (n=40), 2000 (n=40) and 2001 (n=40).

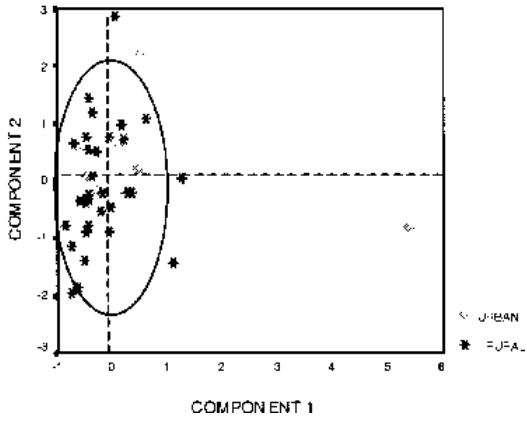


**Figure 3.** Principal component plot of vegetation samples collected in urban (n=10) and rural (n=30) areas of 2001.

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