DIOXIN LEVELS IN AMBIENT AIR MEASUREMENTS IN CATALONIA (SPAIN)

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Introduction

Since the PCDDs/PCDFs can be formed by many antropogenic processes, the presence of these pollutants into the atmosphere is due to several industrial activities. In addition to the emissions from waste management plants, dioxins were also observed in gases emitted from other thermal processes such as sintering plants, hazardous waste incinerators and other diffuse sources ^{1,2}. In 1994, the Environment Department (Departament de Medi Ambientl) of the Catalonia government (Generalitat de Catalunya) in collaboration with the Dioxin Laboratory/Mass Spectrometry Laboratory (Dept.of Ecotechnologies) of the Spanish Council for Scientific Research (CSIC) conducted a surveillance program on polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in ambient air. The study aimed to characterize the dioxin levels in major industrial sites all over the four provinces in Catalonia. Urban, rural areas as well as other presumably non-affected sites were also assessed. Data generated during the study provided a basis for evaluating temporal trends of atmospheric dioxin content at various sites.

Materials and Methods

Samples were collected through the services of the Department of Environment in 25 different sampling points located in Catalonia. The sampling stations are catalogued in agreement with directive $1999/30/CE^{3}$ in two types:

(i) Regarding the emission sources: background (F), traffic (T) and industrial (I) sources.

(ii) Regarding the sampling site location: urban (U), suburban (S), rural (R).

In the majority of the cases the sampling points corresponded to a urban or suburban sites affected by major sources or traffic. A location map of sampling point is given in figure 1. The sampling device consisted in a high volume sampler (HVS). A fiber glass filter was placed on the HVS head followed of a polyurethane foam (PUF) as an adsorbent. The process was controled by spiking the PUF with the same recovery standard ³⁷Cl-2,3,7,8-TCDD. The HVS was connected to a vacumm pump and approximately 1000 m³ of air mass were sucked for 24 h at a sampling speed of 45 m³/h ^{3,4,5}

Prior to the extraction process, the samples were spiked with known amounts of labeled PCDD/PCDF standards described in EPA 1613. All the pollutants were removed from the PUF and the filter by Soxhlet extraction using toluene for 48 h. Finally, extracts were transferred to n-hexane and concentrated prior to the cleanup process.

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Cleanup procedure was based on use of the Power $Prep^{TM}$ system (FMS Inc., MA). The automated system cleanup employs multilayer silica, basic alumina and PX-21 carbon adsorbents, prepackaged in columns made of Teflon and hermetically leaded (FMS Inc. Boston, USA). Purified extracts were analyzed by HRGC-HRMS on a GC 8000 series gas chromatograph (Carlo Erba Instruments, Milan, Italy) equipped with a CTC A 200S autosampler and coupled to an Autospec Ultima mass spectrometer (Micromass, Manchester, UK), using a positive electron ionization (EI+) source and operating in the SIM mode at 10000 resolving power (10% valley definition). Chromatographic separation was achieved with a DB-5 (J&W Scientific, CA, USA) fused-silica capillary column (60 m x 0.25 mm ID, 0.25 m film thickness) with helium as carrier gas in the splitless injection mode (1-2 :L). Quantification was carried out by the isotopic dilution method. The recovery rates of labeled substances were in all cases higher than 85 %. Detailed information is given in reference 6 and 7.

Figure 1. Map of Catalonia. Sampling location points.



Results and Discussion

From 1994 onwards an extensive study of environmental levels of PCDDs/PCDFs was undertaken in Northeast Spain (Catalonia). The study was primarily initated to obtain representative data on different sites potentially affected by industrial activities (i.e.:petroleum refineries and petrochemical industries, power plants, chemical plants and municipal waste incineration plants) or traffic. The findings are given in table 1. The results revealed a variable dioxin content depending

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on both the influence of potential contamination sources and meteorological conditions. Highest levels were ocasionally found in several sampling points affected by industrial activities when anticyclonic conditions occurred. On the other hand, no remarkable differences were found in urban, suburban and rural areas in wind and rain conditions, moreover, the levels were quite below 50 fg I-TEQ/Nm³. In fact, concentrations found in industrial areas varied from 18 to 954 fg I-TEQ/Nm³ with a mean value of 230 fg I-TEQ/Nm³. The findings in urban and suburban varied from 13 to 357 fg I-TEQ/Nm³ with a mean value of 83 fg I-TEQ/Nm³. However, there was a striking difference between the sampling sites affected by traffic ($82 \forall 3 \text{ fg I-TEQ/Nm}^3$) and sites affected by industrial activities ($225 \forall 15 \text{ fg I-TEQ/Nm}^3$). The lowest levels were found in rural areas with levels between 5 and 125 fg I-TEQ/Nm³ with a mean value of 33 fg I-TEQ/Nm³.

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References

1. Fiedler H. (1996) Chemosphere 32, 55.

2. Olie K., Vermeulen PL, Hutzinger O. (1977) Chemosphere 7, 455.

3. Council Directive 1999/30/EC of 22 April 1999 relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air. Official Journal L 163, 29/06/1999, 41

4. Abad E., Caixach J. and Rivera J. (1997) Chemosphere 35, 453.

5. De Jong A.P.J.M., Liem A.K.D. and Hoogerbrugge R. (1993). Chemosphere 27, 73.

6. Abad E., Caixach J. and Rivera J. (2000) J. of Chromatog. 2000, A 893/2, 397.

7. Abad E., Sauló J., Caixach J. and Rivera J. (1997). J. of Chromatog. A 786, 125.

Code	Classification	No. Samples	Min.	Max.	Mean
AF	UT	1	25	25	25
E4	UT	6	13	147	75
15	UT	1	129	129	129
IJ	UT	2	42	78	60
ID	UT	4	68	357	169
13	UT	1	52	52	52
AH	ST	2	67	74	705
A9	ST	6	46	105	88
A6+2404	UI	9	46	618	241
12	UI	4	47	405	180
IB	Ul	2	143	174	158
I 4	UI	6	196	357	264
A7	SI	5	35	306	114
A4	SI	5	18	166	73
AC	SI	4	42	879	357
B1	SI	1	255	255	255
I7	SI	1	243	243	243
16	SI	3	150	954	463
IK	SI	1	348	348	348
IC	SI	3	86	316	174
18	SI	1	132	132	132
A3	RI	13	7	125	48
Al	RI	4	5	32	21
A2	RI	3	43	45	44
1173	RF	1	21	21	21

Table 1. Levels of PCDDs/PCDFs, expressed in fg I-TEQ/Nm³, in ambient air samples collected since 1994 in different sites located in Catalonia.

Background (F), traffic (T), industrial (I), urban (U), suburban (S), rural (R).

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