

TEN YEARS MEASURING PCDDs/PCDFs IN AMBIENT AIR IN CATALONIA (SPAIN)

Gustems Lluís¹, Abad Esteban², Josep Caixach², Albert Manich², Josep Rivera², Rafael Gómez¹, Xavier Guinart¹, Isabel Hernández¹

¹Departament de Medi Ambient de la Generalitat de Catalunya

²Mass Spectrometry Lab., Dept. of Ecotechnologies, IIQAB-CSIC

Introduction

PCDDs and PCDFs can be formed as unwanted by-products in many anthropogenic processes and their presence in the atmosphere comes mainly from several industrial activities which include, for instance, a variety of thermal processes such as waste management plants, cement kiln plants, sintering plants and other diffuse sources¹⁻⁵. Furthermore, once released into the atmosphere, these toxicants can be transported far from their original sources and as a result their presence can be determined in remote areas^{6,7}. In this sense, great efforts have been made to increase the knowledge about these pollutants and stringent regulations aiming to protect public health have already been established.

Monitoring programs play an important role in public and sanitary decisions. In particular, the presence and trend of this pollutants in the atmosphere have been subject of many environmental studies performed all over the world⁸⁻¹³.

In 1994, the Environmental Department (Departament de Medi Ambient) of the Catalanian Government (Generalitat de Catalunya) in collaboration with the Dioxin Laboratory /Mass Spectrometry Laboratory (Dept.of Ecotechnologies) of the Spanish Council for Scientific Research (CSIC) started a surveillance programme on PCDDs/PCDFs in ambient air. The aim of the study was to determine dioxin levels and to assess temporal trends of the atmospheric content of these pollutants in major industrial sites all over Catalonia. Moreover, samples from urban and rural areas as well as other supposedly non-affected sites were also considered. Furthermore, in accordance with the new regulatory framework, a comparison of two different sampling devices, TSP and PM10, has also been performed during the study.

Materials and Methods

177 Samples were collected through the services of the Department of the Environment from 29 different sampling points located in Catalonia (fig. 1). The sampling stations are catalogued in accordance with directive 1999/30/CE into two types: (i) emission sources: background (F), traffic (T) and industrial (I) sources; (ii) sampling site location: urban (U), suburban (S), rural (R). In the majority of cases, sampling points corresponded to urban or suburban sites affected by major sources or traffic¹⁴.

The sampling device consisted of a high volume sampler (HVS) purchased from MCV (Barcelona, Spain). A fibre glass filter was placed on the HVS head followed by polyurethane foam (PUF) as an adsorbent. The process was controlled by spiking the PUF with CSS standard solution (Wellington, Canada) formed by ³⁷Cl-2,3,7,8-TCDD. The HVS was connected to a vacuum pump and between 1000 and 1600 m³ of air mass was collected in 24 h at a sampling flow rate of 45-68 m³/h^{11, 15, 16}.

Prior to the extraction process, the samples were spiked with known amounts of labelled PCDD/PCDF standards (LCS solution, Wellington, Canada). Pollutants were removed from the PUF and the filter by Soxhlet (48 h) using toluene. Finally, extracts were concentrated and transferred to n-hexane prior to the cleanup process. Clean-up procedure was based on the use of the Power PrepTM system (FMS Inc., MA, USA). The automated system clean-up employs multilayer silica, basic alumina and PX-21 carbon adsorbents, prepackaged in Teflon columns and hermetically sealed (FMS Inc. Boston, USA)¹⁷.

Instrumental analysis was performed by HRGC-HRMS on a GC 8000 Series gas chromatograph (Carlo Erba Instruments, Milan, Italy) 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. Detailed information on chromatographic separation and isotopic dilution quantification has been described in previous¹⁹.

Results and Discussion

1.- PCDD/F Monitoring program: In 1994, a comprehensive study on dioxin assessment in ambient air in Northeast Spain (Catalonia) was initiated. The main objective was to get representative data from a wide number of sites potentially affected by industrial activities or traffic exhausts. The results obtained from the analysis of 89 samples, taken at 25 different locations all over Catalonia during a 7 year period, have been reported in previous works^{16, 19}.

ATMOSPHERIC LEVELS, TRANSPORT AND DEPOSITION

Table 1. Levels of PCDDs/PCDFs, expressed in fg I-TEQ/m³, in ambient air samples collected since 1994 in different sites in Catalonia.

Code	Classification	No. of samples	Min.	Max.	Mean 1994-2004
AF	UT	1	25	25	25
E4	UT	7	13	147	69
I5	UT	2	108	129	119
IJ	UT	6	18	82	49
ID	UT	5	33	357	124
I3	UT	2	36	52	44
AB	UT	3	108	223	160
AD	UT	3	21	114	61
AH	ST	7	10	138	52
A9	ST	15	29	105	63
A6	UI	9	46	618	241
I2	UI	5	47	406	161
IB	UI	9	42	174	98
I4	UI	7	168	357	251
A7	SI	10	17	306	69
A4	SI	8	17	165	55
AC	SI	5	43	879	300
B1	SI	4	33	255	158
I7	SI	1	243	243	243
I6	SI	16	24	954	172
IK	SI	1	348	348	348
IC	SI	12	28	316	97
I8	SI	1	132	132	132
AA	SI	9	13	1196	257
A3	SI	16	7	125	46
A1	RI	4	5	32	17
A2	RI	3	43	45	44
1173	RF	1	21	21	21
2404	UF	5	8	28	17

In this work, results generated during the last surveillance program campaign (2001-2003) have been included. Data from more than 87 new samples, taken at the same locations previously considered, allowed assessing recent temporal trends. Other samples were collected in 9 new zones in order to extend and complete the monitoring program. Overall results include 177 samples taken in 29 different sites divided in urban (59 samples in 12 sites), suburban (105 samples in 13 sites) and rural or non-affected areas (13 samples in 3 sites). A summary of the findings is given in Table 1.

As expected, the findings revealed variable dioxin levels depending on both, the influence of potential contamination sources and meteorological conditions. In general terms the new data obtained from the new samples locations did not vary overall results.

A.- Industrial, traffic and background locations: In general, industrial locations presented the highest levels found in this study. Concentrations ranging from 5 to 1196 fg I-TEQ/Nm³, with a mean value of 140 fg I-TEQ/Nm³ and from 10 to 357 fg I-TEQ/Nm³, with a mean value of 72 fg I-TEQ/Nm³ were determined in industrial and traffic sampling points. On the contrary, concentrations from 8 to 28 fg I-TEQ/Nm³, with a mean value of 17 fg I-TEQ/Nm³, were determined in regional background stations. The levels found in urban and suburban stations varied from 8 to 618 and 7 to 1196 fg I-TEQ/Nm³, with a mean value of 112 and 124 fg I-TEQ/Nm³, respectively. The lowest concentrations were found in rural stations, ranging from 5 to 45 fg I-TEQ/Nm³, with a mean value of 28 fg I-TEQ/Nm³.

In particular, the urban areas studied mainly received the impact of road traffic. Six sites were chosen for a dioxin re-evaluation and two more were examined for first time. Finally, four sites typically classified as representative of urban areas with an industrial activity were assessed again. In general, levels in urban areas affected by traffic varied from 103 (AH station) to 357 (zone ID) fg I-TEQ/m³ (n: 25). In particular, zone E4 that was exhaustively evaluated since the beginning of the project because of the presence of two highways and an operating municipal waste incinerator presented a decrease in average I-TEQ levels. In this new study, the values revealed a decrease in the average value from 75 to 69 fg I-TEQ/m³. Special interest was also focussed in station ID, which was chosen as a typical urban area affected by traffic. Previous results revealed a range between 68 and 357 fg I-TEQ/m³ (n: 4) with a mean of 169 fg I-TEQ/m³, obtaining the highest levels at the end of the sampling campaign. This is why this site had been selected to be assessed again and 33 fg I-TEQ/m³ of PCDDs/PCDF levels were found. The most recent results proved again the high variability of the dioxin levels in this point. Finally, two more new sites, sites coded AB and AD (intensive traffic) and catalogued as an urban area affected by traffic were also subject of study. In each case, two samples were collected. The dioxin levels varied from 108 to 223 fg I-TEQ/m³ with an average of 160 fg I-TEQ/m³ in site AB (moderate traffic) and between 21 and 114 fg I-TEQ/m³ with a mean of 61 fg I-TEQ/m³ in AD. In both cases, the dioxin levels are consistent to those found in similar sites. Regarding urban areas affected by industrial activities, seven more samples were collected in sampling sites coded as I2 and IB. In both cases, the results revealed a decrease in the average value about 11% and 31% respectively (Table 1).

B.- Urban, suburban and rural locations: In sampling areas classified as suburban, a total of 112 samples were collected in 13 different sites, two of which were affected by traffic and the rest by industry. Forty-six samples were collected from 1994 to 2000 and 74 samples more up to 2003. In general, levels in suburban areas ranged between 5 (code A1) and 1196 (code AA) fg I-TEQ/Nm³. Nevertheless, as expected, the highest levels were determined in industrial sites, whereas traffic areas presented levels ranging from 10 (AH) to 357 fg I-TEQ/m³ (ID). The most remarkable point was a decrease in the average values in the two areas affected by traffic when comparing with data reported up to 2000. The average values decrease from 70 to 52 (AH) and from 88 to 63 (A9) fg I-TEQ/m³. However, these findings are comparable or slightly lower to those found in urban areas.

Regarding suburban areas affected by industrial activities, 74 new samples were collected in the period between 2000 and 2002. In general, the highest values have been detected in these kind of zones, being the point coded as AA the most contaminated one (1196 fg I-TEQ/m³). In this sense, five points specially examined in previous studies (codes A7, AC, B1, I6 and IC) presented a decrease in the average values in the new sampling period. However, sampling codes A4 presented levels slightly higher in comparison with the ones found in previous campaigns. Finally, four samples were collected at sites coded I7, IK and I8 for the first time. The results revealed

significant dioxin content in ambient air with concentrations between 132 and 348 fg I-TEQ/m³. These zones will, thus, be subject to future evaluation.

Rural and background areas were also subject of study. Eight samples collected in three different sites revealed overall results ranging from 5 to 45 fg I-TEQ/m³ with a mean of 28 fg I-TEQ/m³, whereas background stations (code 1173 and 2404) presented levels of 8 to 28 fg I-TEQ/m³. In general, overall results are comparable to those reported in other works^{8, 11, 12}.

2.- TSP and PM10 sampler comparison: In accordance with present regulatory framework regarding limit values for some pollutants in ambient air, a comparison between two different samplers has also been carried out during this study. Thus, forty-eight samples were collected at several places in fourteen sampling campaigns using both, TSP and PM10 samplers. The main difference between these two devices refers to the size of the particles that can reach the filter surface. The TSP sampler allows trapping the whole particulate, while in the PM10 system only particles with a size below 10 µm can be collected.

Statistical data analysis: The amounts of 2,3,7,8 PCDDs, PCDFs, ΣPCDD/Fs and I-TEQs of the 24 sample points collected from 8 locations at different dates, using both the PST and PM10 methods, were tested in order to determine if they were equivalent examining its statistical distribution by means of the Chi-Square and the Kolmogorow-Smirnov tests.

Based on the normalized results, a two-way ANOVA were applied with the objective to determine the differences between the above results obtained by the PST and the PM10 methods at different locations.

Finally the equivalence of both methods were tested by comparing the relative amount of 2,3,7,8 PCDD/F congeners collected by both devices using the Contingency Tables method considering the congeners as the rows and the methods as the columns of the contingency table. The Chi-square test performs a hypothesis test to determine whether or not to reject the idea that the row and column classifications are independent. If they were, the amount of a particular congener may bear no relation to the collecting method. A probability of 0.05 or lower was considered significant.

Results: The statistical distribution of PCDDs, PCDFs, ΣPCDD/Fs and the I-TEQs followed the lognormal distribution, therefore, in order to apply the statistical parametric methods the results were taken as logarithms.

By the application of a two-way ANOVA considering the influence of the location (and date) and the collecting method on PCDDs, PCDFs, ΣPCDD/Fs and I-TEQs taken as logarithms, it was observed that the location and date gave statistically significant differences as expected, but non statistically significant differences were observed between methods on PCDFs and I-TEQs results. The significant level of the differences is summarized in Table 1.

Table 1: Significant level of the differences between location (and date) and collecting methods on 2,3,7,8 PCDFs, PCDDs, ΣPCDD/Fs and I-TEQs obtained by the application of a two-way ANOVA on the logarithms of the original data.

Source of variation	PCDFs	PCDDs	PCDD/Fs	I-TEQs
Location and date	0.1%	0.1%	0.1%	0.1%
Methods	NS	0.1%	1.0%	NS

Figure 1 shows the results of the Log (I-TEQ) according to the location (date) and method. The thin line (PM10 method) and the thick line (PST method) are overlapped and consequently, there is not a clear effect of the method on the results. Similar plot should be observed considering the PCDFs amount, while in relation with PCDDs and ΣPCDD/Fs the results of the PST methods would be higher than those obtained by the PM10 method.

Being that the methods were equivalent as regards to the I-TEQs, the equivalence was also tested considering the relative amount of congeners using the Contingency Tables test. The significant level of the Chi-square parameter allows supporting in 19 cases of 24 the hypothesis that the collecting method does not influence the differences between congeners.

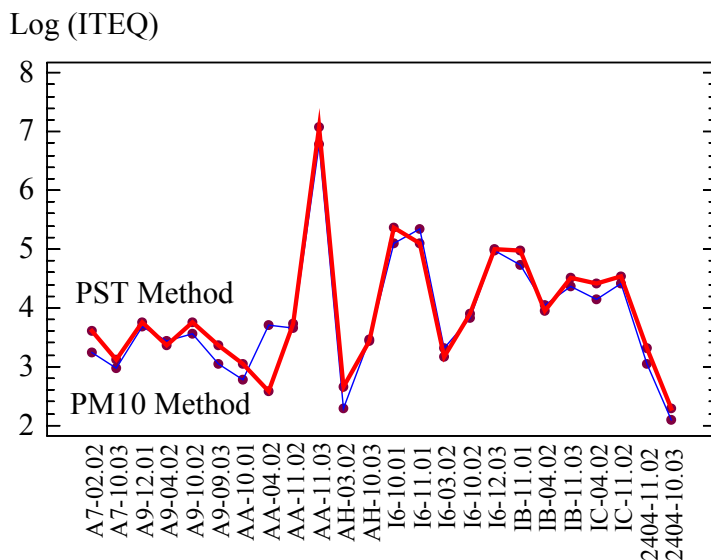


Figure 1: I-TEQs in logarithms according to the different locations (and dates) and the method used. The thick line connects the results obtained by the PST method, while the thin one connects the results obtained by the PM10 method.

Just in five cases, two of them corresponding to the location AA (04.02 and 11.03), showed differences mainly between the most chlorinated congeners that could be attributed to the collecting

method. The remaining three cases corresponding to the location I6 (11.01, 03.02 and 12.03) showed differences between the same congeners that could be attributed to the collecting method.

Although more samples should be analysed to obtain concluding results, data obtained until now showed that levels given by the two sampling systems are comparable or those from the PM10 are a bit lower. Only five cases presented clearly higher levels using PM10 compared with those found with TSP sampler.

Acknowledgements

The authors wish to thank Ms M. G. Martrat and Mr M.A. Adrados for sample preparation and Mr Jordi. Sauló for the mass spectrometric analyses.

References

1. Ballschmiter, K., Buchert, H., Niemczyk, R., Munder, A. Swerev, M., 1986. *Chemosphere* 15, 901.
2. Hagenmaier, H., Lindig, C., She, J., 1994. *Chemosphere* 29, 2163.
3. Fiedler H., 1996. *Chemosphere* 32, 55.
4. Rappe, C., 1994. *Fresenius J. Anal. Chem.* 348, 63.
5. Lohmann, R., Jones, K.C., 1998. *Science Total Environ.* 219, 53.
6. Lohmann, R., Gree J.J.L., Jones, K.C., 1999. *Science Total Environ.* 33, 4440.
7. Baker, J.I., Hites R. A., 1999. *Environ. Sci. Technol.* 33, 14.
8. Fiedler, H., Rottler, H., Peichl, L., Knetsch, G., Basler, A. 2000. *Organohalogen Compd.* 45, 264.
9. Sin, D.W., Choi, J.Y. and Louie, P. K., 2002. *Chemosphere* 47, 647.
10. Stenhouse, I.; Moncur, J.; Kocan, T.; Violova, A., 1998. *Organohalogen Compd.* 39, 77.
11. Bolt, A., de Jong, A.P.J.M., 1993. *Chemosphere* 27, 73.
12. Cleverly, D. H., Winters, D., Ferrario, J., Schaum, J., Schweer, G., Buchert, J., Greene, C., Dupuy, A., Byrne, C., 2000. *Organohalogen Compd.* 45, 248.
13. Cleverly, D.H., Winters, D., Ferrario, J., Schaum, J., Riggs, K., Hartford, P., Joseph, D., Wisbith, T., Dupuy, A., Byrne, C., 2001. *Organohalogen Compd.* 51, 1.
14. 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
15. European Standard EN 12341. Air quality - Determination of the PM10 fraction of suspended particulate matter - Reference method and field test procedure to demonstrate reference equivalence of measurement methods. Brussels, 1998.
16. Abad, E., Caixach, J., Rivera, J., 1997a. *Chemosphere* 35, 453.
18. Abad, E., Caixach, J., Rivera, J., 2000. *J. of Chromatog.*, A 893/2, 383.
17. Abad, E., Caixach, J., Rivera, J. 1997b. *J. of Chromatog.* A 786, 125.
19. Abad, E., Martrat, M.G., Caixach, J., Rivera, J., Gustems, Ll., Massagué, G. and Puig, O. et al., 2001. *Organohalogen Compd.* 51, 112.