ANALISYS OF PCDD/PCDF FROM EMISSIONS SOURCES AND AMBIENT AIR IN NORTHEAST OF SPAIN

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Summary. PCDD/PCDF have been detected and quantified in emissions from municipal and industrial waste incinerators. At the same time, levels of PCDD/PCDF in ambient air were measured in order to evaluate the possible influence. Identification and quantification were carried out by HRGC/HRMS with isotopic dilution as quantification method.

INTRODUCTION.

Polychlorodibenzo-p-dioxins and polychlorodibenzofurans (PCDD/PCDF) are two series of chlorinated polyciclyc aromatic compounds with similar properties which have attracted the interest of many laboratories all over the world because of their toxicity and bioacumulative properties and as potential hazard for human health. Since 1977, when Olie[1] indicated dioxins presence in municipal waste incinerator (MWI) emissions, these compounds have been the subject of many environmental studies. Liem[2] found high levels of dioxins in cow´s milk from the vicinity of MWI and other dioxins sources. Afterwards, de Jong[3] stated that PCDD/PCDF levels were influenced by their vicinity to an incinerator depending on wind trajectories, and Rappe[4] indicated a typical pattern from combustion sources. Due to extremely low levels compared to potencially interfering compounds the analysis of PCDD/PCDF is complex and very time-consuming. In order to remove the possible interferences sample extraction, clean-up procedure, detection and quantification by high resolution gas chromatography coupled to high resolution mass spectrometry using the isotopic dilution technique have been used[5,6].

In Spain, CSIC has developed the required methodology to analyze PCDD/PCDF in several matrices which involves biological and environmental studies[7,8]. The aim of this work has been to evaluate the levels of PCDD/PCDF emitted to the atmosphere through municipal waste incinerator (MWI) and their eventual impact on the levels in ambient air near their zone of influence. Samples were collected in northeast Spain (Catalunya).

EXPERIMENT

Sampling:

Stack gas samples were collected using a filter, condenser, adsorbent sampling system. Sampling recovery standard (^{37}Cl-2,3,7,8-TCDD) was used spiking the particulate filter prior to sampling the stack gases. The sampling train was operated isokinetically, with the probe thermostated to the stack gas temperature and the filter unit at 120°C. XAD-2 resin was used as adsorbent trap for organic pollutants and was cooled using recirculated water. Ambient air samples were collected with a high volume sampler using

fiber glass filter and polyurethane foam (PUF) as sorbent, which were spiked with the same recovery standard.

Extraction:

Samples were spiked with ^{13}C- labelled standards from CHEMSYN Science Laboratories (Lennexa, USA) before soxhlet extraction. All pollutants were removed from solid matrices (filter, PUF or XAD-2 resine) using toluene for 48 h. At the same time, liquid-liquid extraction was performed to extract these compounds from condensed water. Afterwards, the extract from solid matrices and liquid extraction were mixed and concentrated prior to cleanup process.

Clean-up:

Cleanup process was based on liquid-solid adsorption chromatography in glass column at atmospheric pressure[5,6]. Every step was controlled by GC-ECD

1. Multilayer silica column coupled to a florisil column:
This column was composed of sequential layers of $Na_2SO_4|SiO_2|SiO_2$-$H_2SO_4|SiO_2|SiO_2$-$NaOH|SiO_2|SiO_2$-$AgNO_3$ coupled to a florisil column. The interferences were eluted with n-hexane. Afterwards multilayer silica column was disassembled and florisil column was eluted with a mixture of toluene:eter. This fraction contains the PCDD/Fs.

2.Basic alumina column:
Basic alumina from ICN Super I (50-200 mesh) was used. Interferences in this case were eluted in the first fraction using n-hexane and mixture of n-hexane/dichloromethane (98:2) in separate runs. PCDD/Fs were eluted with a mixture of dichloromethane/n-hexane (1:1).

***Analysis by* HRGC/HRMS:**

Gas chromatograph:	CE 8000 series	
Mass spectometer:	Autospec Ultima (Fisons instruments)	
Column:	**JWDB-5 and JWDB-DIOXIN**, 60m length, 0.25 µm inner diameter and 0.25 µm film.	
Temperature.	**DB-5:**	140°C (1min) $\xrightarrow{20°C/min}$ 200°C (1min) $\xrightarrow{3°C/min}$ 300°C (20 min)
	DB-DIOXIN:	140°C (1min) $\xrightarrow{20°C/min}$ 200°C (3 min) $\xrightarrow{2°C/min}$ 270°C (85 min)
Injection:	Splitless, 1-2 µL, at 280°C (DB-5) and 270°C (DB-DIOXIN)	
Carrier gas:	Helium (v: 35 cm/s; T: 100C)	
Analyser mode:	SIR Voltage	
Resolution:	10.000	
Ionization Mode:	EI+, at 37 eV	

Results and Discussion

Sources of dioxins and furans were controlled over the last three years: 4 waste incinerators and 2 industrial incinerator. The results of levels from emissions of 2,3,7,8 - substituted PCDD/F are summarized in table 1:

table 1. Results of PCDD´s and PCDF´s emitted *

	MWI - 1 (ng/Nm³)	MWI - 2 (ng/Nm³)	MWI - 3 (ng/Nm³)	MWI - 4 (ng/Nm³)	IWI - 1 (pg/Nm³)	IWI - 2 (pg/Nm³)
2,3,7,8-TCCD	0.20	0.11	0.42	0.05	3.92	10.71
1,2,3,7,8-PeCDD	0.49	0.35	3.21	1.17	23.96	19.18
1,2,3,4,7,8-HxCDD	0.45	0.24	6.65	2.22	30.81	22.03
1,2,3,6,7,8-HxCDD	0.71	0.46	8.72	4.08	60.19	43.63
1,2,3,7,8,9-HxCDD	0.69	0.69	7.06	2.35	156.06	18.47
1,2,3,4,6,7,8-HpCDD	6.41	1.90	115.18	51.59	368.05	289.19
OCDD	18.18	2.21	120.27	91.39	1036.09	648.90
2,3,7,8-TCDF	1.41	2.39	1.78	0.5	183.58	85.44
1,2,3,7,8-PeCDF	1.33	0.64	2.91	1.11	206.24	46.78
2,3,4,7,8-PeCDF	1.94	0.99	12.97	2.10	179.36	71.73
1,2,3,4,7,8-HxCDF	2.69	1.64	25.19	4.12	608.31	193.52
1,2,3,6,7,8-HxCDF	2.74	0.98	30.05	4.33	475.11	108.56
1,2,3,7,8,9-HxCDF	4.50	0.99	14.002	12.01	293.46	246.05
2,3,4,6,7,8-HxCDF	0.26	0.06	45.43	0.45	95.38	14.13
1,2,3,4,6,7,8-HpCDF	14.44	2.67	268.90	101.16	1851.03	487.73
1,2,3,4,7,8,9-HpCDF	2.34	0.34	38.38	20.02	419.88	66.30
OCDF	13.82	3.49	295.93	81.41	3023.86	1251.59
Total TCDD	2.64	2.09	15.30	25.39	537.92	810.84
Total PeCDD	4.55	4.76	37.40	44.20	2161.42	468.71
Total HxCDD	7.90	6.22	103.80	74.57	1085.15	639.91
Total HpCDD	12.47	3.32	220.90	98.68	818.61	607.60
Total TCDF	32.29	21.16	80.50	22.19	2435.05	646.07
Total PeCDF	24.84	13.23	184.90	33.51	3775.26	701.77
Total HxCDF	36.19	12.74	435.90	190.97	8562.70	1145.45
Total HpCDF	33.53	5.47	570.60	305.73	14411.96	1163.65
No. Samples	20	7	3	2	4	3
Mean (I-TEQ ng/Nm³)	3.26	1.67	27.18	6.65	0.14	0.34
Range (I-TEQ ng/Nm³)	4.85-0.65	3.26-0.88	29.95-23.79	15.5-4.15	0.61-0.1	0.6-0.01
I-TEQ (g/year)	**1.96**	**1.74-1.48**	**10.19**	**4.99**	**12.75(mg/year)**	**1.5(mg/year)**
Output Flow Gas (m³/h)	80.000	100.000-120.000	50.000	100.000	5.000	1.400

* *Data mean values.*

Levels of PCDD's and PCDF's in ambient air in differents influence zones, including rural air, urban air and possible MWI zones, are pointed out in table 2.

table 2. Results of PCDD's and PCDF's in ambient air *

	Zone 1 (pg/Nm³)	Zone 2 (pg/Nm³)	Zone 3 (pg/Nm³)	Zone 4 (pg/Nm³)	Zone 5 (pg/Nm³)	Zone 6 (pg/Nm³)	Zone 7 (pg/Nm³)	Zone 8 (pg/Nm³)
2,3,7,8-TCCD	0.026	0.006	0.003	0.007	0.010	0.007	0.005	0.040
1,2,3,7,8-PeCDD	0.031	0.009	0.010	0.014	0.050	0.020	0.010	0.045
1,2,3,4,7,8-HxCDD	0.029	0.008	0.013	0.013	0.060	0.040	0.010	0.100
1,2,3,6,7,8-HxCDD	0.064	0.023	0.027	0.020	0.155	0.103	0.015	0.150
1,2,3,7,8,9-HxCDD	0.076	0.031	0.043	0.033	0.210	0.150	0.020	0.140
1,2,3,4,6,7,8-HpCDD	0.385	0.218	0.277	0.223	1.720	0.867	0.135	1.035
OCDD	1.110	1.286	0.803	1.237	5.695	2.313	0.770	2.920
2,3,7.8-TCDF	0.105	0.042	0.313	0.273	0.535	0.377	0.205	0.350
1,2,3,7,8-PeCDF	0.055	0.012	0.030	0.020	0.115	0.027	0.015	0.225
2,3,4,7,8-PeCDF	0.116	0.029	0.063	0.047	0.230	0.127	0.035	0.410
1,2,3,4,7,8-HxCDF	1.029	0.046	0.180	0.127	0.595	0.413	0.080	0.480
1,2,3,6,7,8-HxCDF	0.075	0.027	0.073	0.050	0.210	0.217	0.030	0.425
1,2,3,7,8,9-HxCDF	0.094	0.035	0.097	0.077	0.315	0.387	0.040	0.450
2,3,4,6,7,8-HxCDF	0.009	0.004	<0.001	0.003	0.015	0.020	<0.001	0.020
1,2,3,4,6,7,8-HpCDF	0.298	0.120	0.387	0.287	3.425	1.380	0.220	1.300
1,2,3,4,7,8,9-HpCDF	0.045	0.016	0.043	0.033	0.335	0.200	0.020	0.110
OCDF	0.128	0.126	1.213	1.810	126.815	4.090	1.550	0.755
Total TCDD	0.600	0.332	0.333	0.357	0.815	0.897	0.490	1.400
Total PeCDD	0.472	0.281	0.493	0.187	1.455	1.137	0.375	2.015
Total HxCDD	0.766	0.284	0.550	0.387	2.245	2.220	0.325	2.965
Total HpCDD	0.673	0.360	0.623	0.503	3.465	1.867	0.335	2.355
Total TCDF	1.530	0.716	1.680	1.803	3.490	2.497	1.405	5.315
Total PeCDF	0.744	0.269	0.917	0.597	2.715	1.500	0.545	3.975
Total HxCDF	1.909	0.309	1.320	0.727	4.115	3.180	0.475	2.520
Total HpCDF	0.628	0.248	0.873	0.600	6.645	3.317	0.420	1.665
No. Samples	8	12	3	3	2	3	2	2
Mean (I-TEQ pg/Nm³)	**0.28**	**0.05**	**0.13**	**0.20**	**0.55**	**0.28**	**0.08**	**0.52**
Range (I-TEQ pg/Nm³)	0.62-0.05	0.5-0.01	0.15-0.11	0.43-0.07	0.95-0.15	0.36-0.20	0.01-0.05	0.88-0.16

* *Data mean values.*

Zone 1: Urban air with high traffic influence
Zone 2: Rural air, near MWI-1
Zone 3: Urban air
Zone 4: Urban air
Zone 5: MWI-3 influence zone
Zone 6: MWI influence zone (without dates), high traffic and industrial influence
Zone 7: High industrial activity, nearly industrial incinerators 5
Zone 8: High industrial activity, nearly industrial incinerators 6

fig 1. Isomer distribution patterns from municipal waste incinerator, using DB-5 column.

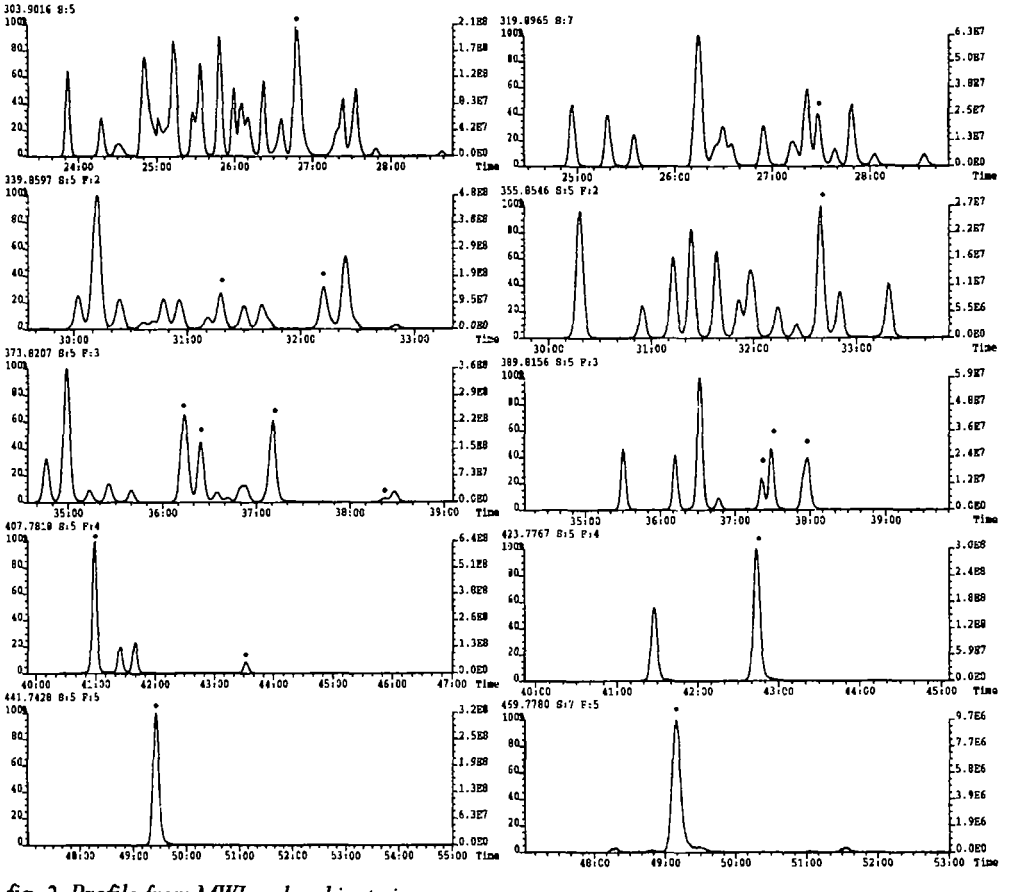
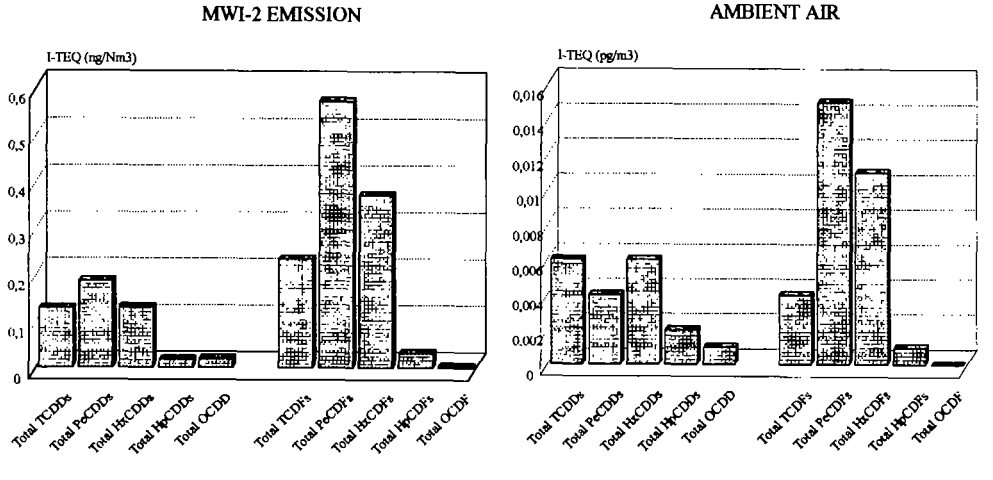


fig. 2. Profile from MWI and ambient air.



The mean values of the toxicity equivalents calculated for each group of samples are: 0.65-29.95 ng I-TEQ/Nm^3 for MWI, the higher value corresponding to the lower efficiency of the stack gas cleaning in the older installations. Values for the IWI are in the range of 0.01-0.61 ng I-TEQ/Nm^3, often complying the limit of 0.1 ng I-TEQ/Nm^3.

Ambient air determinations range is 0.05-0.55 pg I-TEQ/Nm^3. The air maximun corresponds to zones 5 with the eventual influence of an old MWI, emitting high levels of PCDD/PCDF, and zone 8 with an important chemical industry. Zones 1, 3 and 4 considered as urban areas, with traffic as the main source, exhibit similar levels, ranging between 0.13 and 0.28 pg I-TEQ/Nm^3.

Patterns of homologues from incinerators (fig. 1) are similar as expected, independently of the gas cleaning method used in the installation. Profiles of ambient air samples from areas supposed to be influenced by incinerators present the same aspect than stack emissions (fig. 2).

The estimation of the total PCDD/PCDF emitted to the atmosphere by the measured MWI in Catalunya is of the order of 20 g I-TEQ/year. Data from the biggest incinerator operating with an obsolete gas cleaning technology are not available. Observed results are in good agreement with the most recent data reported in the literature[9,10,11,12,13]. Further improvements in the gas cleaning systems to attain the 0.1 ng I-TEQ/Nm^3 target of the MWI should greatly reduce the total amount of PCDD/PCDF released into the atmosphere.

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REFERENCES

1. K. Olie, P.L: Vermeulen, O. Hutzinger. Chemosphere 6, 455-9 (1977).
2. AKD Liem, R. Hooger , R.R. Kootstra. Chemosphere Vol. 23 No. 11-12 pp 1675-84 (1991).
3. Bolt A. de Jong APJM. Chemosphere, Vol. 27 No. 1-3 pp. 73-81, (1993).
4. Rappe C. Fresenius J. Anal. Chem. (1994) 348: 63-75.
5. Proposed reference method for the determination of PCDD/PCDF in pulp and paper mill effluents by Chemistry Division, River and Road Environmental Technology Centre, Conservation and Protection. Environment Canada (1990).
6. EPA. Method 1613: Tetra- through Octa-chlorinated Dioxins and Furans by isotopic dilution HRGC/ HRMS.
7. J. Rivera. Fresenius J. Anal. Chem. (1994) 348: 167-170.
8. Gonzalez, M.J., Rivera J. Chemosphere, Vol. 27, No. 1-3, pg. 97-104, 1993.
9. Djem Liem. Environment Scienc. & Pollut. Res 2(1) 46-56 (1995).
10. Hagenmeier, H. Chemosphere, Vol. 29 Nos. 9-11, pp. 2163-2174, 1994.
11. A. de Jong, Journal of Chromatography, 643 (1993), 91-106.
12. Wassermann, E.. Chemosphere, Vol. 20, No. 5 pp. 907-913 (1995).
13. H. Fiedler. Chemosphere, vol. 32 No. 1 pp. 55-64 (1996).