DIOXIN ASSESSMENT IN COAL-FIRED POWER STATIONS FROM SPAIN

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Introduction

Polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) enter the environment in ultra-trace amounts from various combustion and industrial sources and as chemical impurities in technical formulations. Some combustion processes have been widely studied: municipal waste and hospital incinerators or domestic heatings. However, scarce information about big heating furnaces as coal-fired power stations is available. The aim of this study was to evaluate the levels of PCDD/Fs emitted from five coal-fired power plants in Spain. Due to few stack national and european measurements available, this work is a first approximation to the actual levels of PCDD/Fs from coal-fired power stations in Spain.

Methods and Materials

In this work five Spanish power stations, representing approximately 45 % of the national coal-fired power generation[1], were studied during 1997 and 1998. In general terms, these plants presented production capacities ranging between 80 and 350 MW and they burned different types of coals. Four plants (A-D) use a conventional coal-fired technology with electrostatic precipitators as pollution control device, while E is a pressurised fluidised bed power plant.

To perform the study, sampling process, extraction, clean-up and analysis fulfilled the minimum requirements described in the European Standard EN-1948:1996[2]. Sampling was carried out with a stack gas sampler of filter/condenser method. Firstly, two samples were taken in the power station A (A-1 and A-2) to check if sampling process agrees with the European Standard EN 1948:1. Then a sample was collected in each power plant (A-3, B, C, D and E). Table 1 summarises information on each sample campaign.

Analytes were separated from the samples by Soxhlet extraction using toluene for 48 h. The clean-up was based on the classic liquid-solid adsorption chromatography and was performed with an automated Power Prep™ system using multi-layer silica, basic alumina and PX-21 carbon adsorbents pre-packaged in columns (FMS Inc., USA)[3]. Purified extracts were analysed by HRGC-HRMS on a GC 8000 series gas chromatograph (Carlo Erba Instruments, Italy) equipped with a CTC A200S autosampler and coupled to an Autospec Ultima mass spectrometer (Micromass, UK). Chromatographic separation was achieved with a DB-5 (J&W Scientific, USA) fused-silica capillary column (60 m x 0.25 mm ID x 0.25 mm). As confirmation, a DB-DIOXIN (J&W Scientific, USA) fused-silica capillary column (60 m x 0.25 mm ID x 0.25 mm) was employed when required[4].

Table 1. Sample collection campaign of PCDDs/PCDFs determination from coal-fired power stations.

Sample	Date	Volume (Nm^3, 11% O_2)	Particles (mg)
A1	10/27/97	10.6	412
A2	10/30/97	10.8	318
A3	24/3/97	10.1	456
B	3/4/98	7.3	421
C	23/4/98	10.4	780
D	31/3/98	11.4	257
E	21/4/98	9.4	133

Results and Discussion

Table 2 shows the concentrations, expressed as pg /Nm^3, found in the different samples. The total i-TEQ levels ranged from 0.05 to 0.89 pg/Nm^3. These values are far from those found in the emissions of municipal wastes and hospital incinerators (2-20 ng/Nm^3) reported in previous inventories and below of the established limit of 100 pg i-TEQ/Nm^3 adopted by many industrialised countries.

Table 2. PCDD/F concentrations (pg/Nm^3) in emissions of coal-fired power stations.

	A1	**A2**	**A3**	**B**	**C**	**D**	**E**
2,3,7,8-TCDF	0.39	‡ (0,04)	0.47	0.80	0.25	0.1	0.35
1,2,3,7,8-PeCDF	‡ (0,16)	‡ (0,03)	‡ (0,06)	‡ (0,01)	‡ (0,05)	0.27	0.29
2,3,4,7,8-PeCDF	‡ (0,15)	‡ (0,04)	‡ (0,07)	‡ (0,12)	‡ (0,05)	0.37	0.17
1,2,3,4,7,8-HxCDF	‡ (0,09)	‡ (0,08)	0.33	0.97	‡ (0.27)	0.86	0.34
1,2,3,6,7,8-HxCDF	‡ (0,10)	‡ (0,08)	0.13	0.46	‡ (0.13)	0.48	0.13
2,3,4,6,7,8-HxCDF	‡ (0,11)	‡ (0,09)	0.30	0.28	‡ (0.20)	0.77	0.27
1,2,3,7,8,9-HxCDF	‡ (0,15)	‡ (0,11)	‡ (0,12)	‡ (0,12)	‡ (0,109	0.12	‡ (0,08)
1,2,3,4,6,7,8-HpCDF	‡ (0.75)	0.41	1.00	1.66	0.69	2.72	1.07
1,2,3,4,7,8,9-HpCDF	‡ (0,15)	‡ (0,24)	0.29	0.22	‡ (0,16)	1.16	0.3
OCDF	‡ (2.95)	2.07	2.38	2.08	0.89	7.93	2.35
2,3,7,8-TCDD	‡ (0,07)	‡ (0,06)	0.13	‡ (0,24)	‡ (0,02)	‡ (0,02)	‡ (0,05)
1,2,3,7,8-PeCDD	‡ (0,33)	‡ (0,30)	‡ (0,09)	‡ (0,08)	0.32	‡ (0,22)	‡ (0,09)
1,2,3,4,7,8-HxCDD	‡ (0,15)	‡ (0,11)	‡ (0,11)	‡ (0,14)	‡ (0,09)	0.19	‡ (0,079
1,2,3,6,7,8-HxCDD	‡ (0,20)	‡ (0,14)	0.47	0.4	0.22	0.45	0.57
1,2,3,7,8,9-HxCDD	‡ (0,18)	‡ (0,13)	‡ (0,10)	‡ (0,13)	0.21	0.37	0.32
1,2,3,4,6,7,8-HpCDD	48.51	2.48	1.94	1.65	1.26	2.17	2.92
OCDD	385.10	19.54	10.02	9.59	7.00	8.75	0.22
Total i-TEQ	0.89	0.05	0.35	0.27	0.29	0.34	0.62

‡ Not detected or quantifed. Detection limits are presented in brakets.

All plants show similar i-TEQ over 0.3 pg/Nm^3, except the plant E and the first sampling of plant A that present higher levels: 0.62 and 0.89 pg/Nm^3 respectively. However no clear conclusions about the influence of the combustion conditions can be extracted, because levels determined in the three samplings on plant A are affected by a strong source of variation. In comparison, our values are lower than those reported by Riggs *et al.*[5] from U.S coal-fired power plants ranged between 0-200 pg/Nm^3. These emissions and their emissions factors (Figure 1) are much lower than those reported for less efficient combustions, like heating furnaces or industrial sources, estimated between 1.6-2500 ng i-TEQ/kg coal[6]. The reasons of low PCDD/Fs levels in coal combustion emission in comparison with waste combustion seem to be related with SO_2 and trace metals levels and combustion conditions, specially temperature combustion which is usually higher in power generation processes.

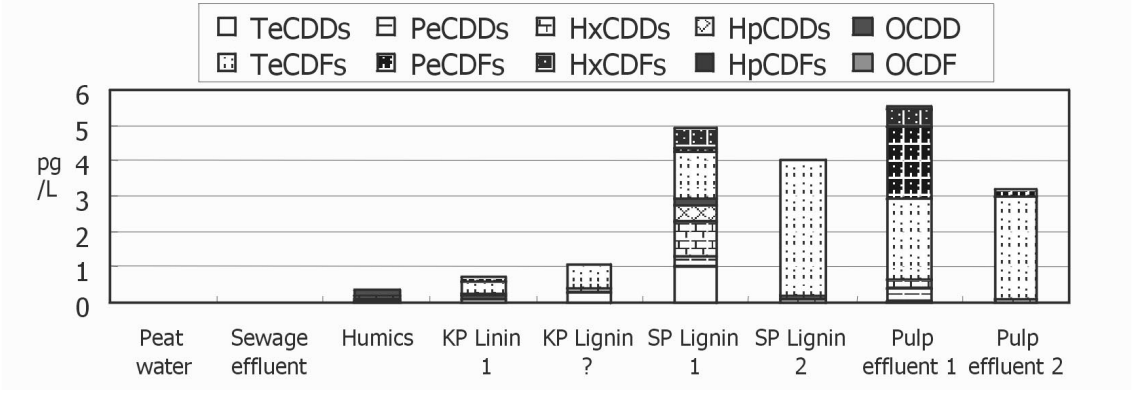

Figure 1. Estimated emission factors in pg i-TEQ/ kg coal.

The absolute concentrations of D power plant are also the highest for most of isomers, while the plant C presents the lowest contents. Octachloro-substituted isomers, both furans and dioxins, are the most abundant. OCDD concentrations range from 7 to 10 pg/Nm^3, except for the plant E that shows very low levels. The OCDF present levels between 2 and 4 pg/Nm^3, in this case the plant D shows a peak of 8.75 pg/Nm^3. Hepta-substituted compounds are the second family on importance, remaining compounds are in lower concentrations and even the 2,3,7,8-TCDD has been only detected in one of the samples taken in the plant A.

Figure 2 shows the estimated annual PCDD/Fs emissions from studied coal-fired plants. These data can be used to estimate the annual PCDD/Fs from coal-fired power generation in 0.86 g i-TEQ/year in Spain. These data present a similar magnitude to those reported in the European Dioxin Emission Inventory[7]. This document reported ranges of concentration for different countries, for example: 1.5-2.5 g i-TEQ/year in Belgium, 0.1-0.13 g i-TEQ/year in Switzerland, 5 g i-TEQ/year in Germany, 1.44-2 g i-TEQ/year in Denmark, 2 g i-TEQ/year in France. The value assigned for Spain is 3.9 g i-TEQ/year, but the origin of this value is not sufficiently explained and it can be probably based in overestimated emission factors from less efficient combustions.

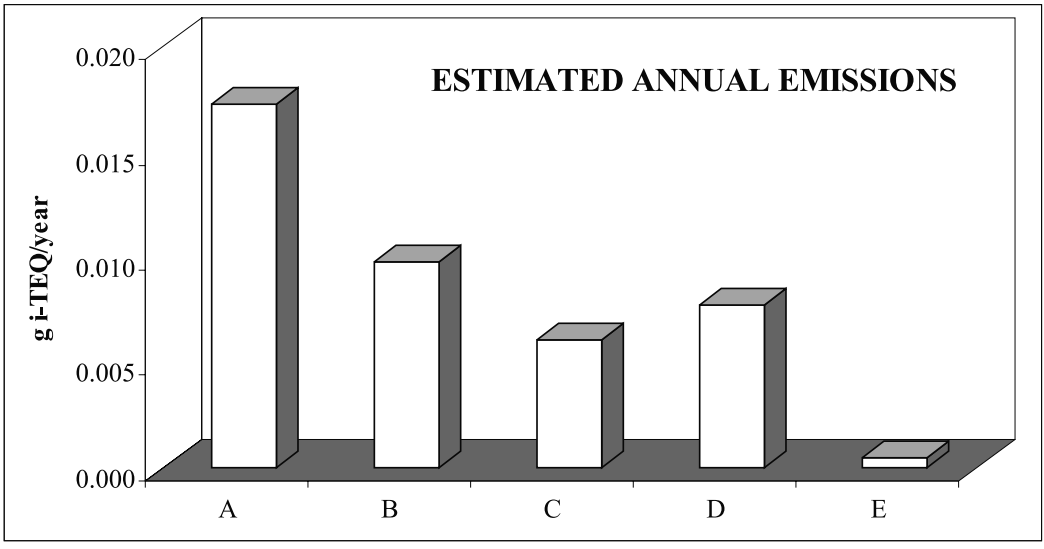

Figure 2. Estimated annual PCDD/Fs in studied coal power plants.

Acknowledgements

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