PCDD/F EMISSIONS IN POWER GENERATION PLANTS: EVALUATION IN THE FRAME OF SPANISH DIOXIN INVENTORY

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Introduction

In general terms, combustion constitutes an oxidation process in which basically chemical reactions transform carbon species into CO_2. Hence, the carbon cannot be totally converted into CO_2 and minor amounts of unwanted products of incomplete combustion and toxic pollutants are to be found. Concretely, polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) enter the environment in ultra-trace amounts from various combustion sources. Although some of these combustion processes have already been widely studied, such as municipal waste incinerators, scarce information is available about big heating furnaces as the related to power generation stations.

Many countries have recently compiled national inventories of PCDD/F emissions to air from regulated, energetic and industrial sources in order to gain a better understanding of the quantities released per annum and to develop strategies to reduce emissions. In February 1993 the European Council of Ministers set the political goal to achieve a 90 % reduction of dioxin emissions from known sources by the year 2005 as compared to the reference 1985 year. To achieve this ambitious aim, an inventory of all relevant emission sources and an estimate of the total emissions in the member states are required. The community strategy for these compounds stimulates identification of dioxin sources and their quantification in specific ones.

According to this strategy Spain is carrying out a national inventory of dioxin sources and power generation sector was considered an interesting activity to be researched as a dioxin source. Consequenty, some of their plants have been studied during a 2003-2005 Spanish monitoring program.

Data obtained in this survey, corresponding with different matrices: flue gas and fly ash, and the preliminary emission factors for air releases from eleven power generation plants are presented. Additionally, the PCDD/F content related to some fuels is attached.

Methods and Materials

In the frame of the Spanish dioxin inventory, eleven power generation stations, at different locations spread in the national geography, were evaluated during 2003-2005 years. In general terms, they presented production capacities ranging between 125 and 800 MWh and they burned three different types of fuel: coal, natural gas and fuel oil.

To perform the study, sampling processes, extraction, clean-up and analysis fulfilled the minimum requirements described in the European Standard EN-1948:1996. Sampling was carried out with a stack gas sampler filter condenser method. Table 1 summarizes information about each sample campaign and matrices evaluated.

Table 1. Information about sample campaigns and matrices evaluated.

REFERENCE	TYPE OF FUEL	VOLUME (Nm^3, 10 % O2)	TYPE OF SAMPLE		
1	coal	11,15	flue gas	fly ash	coal
2	coal	10,38	flue gas	fly ash	coal
3	coal	10,84	flue gas	fly ash	coal
4	coal	11,20	flue gas	fly ash	coal
5	coal	8,95	flue gas	fly ash	*
6	coal	10,30	flue gas	fly ash	coal
7	coal	11,49	flue gas	fly ash	coal
8	coal	8,89	flue gas	fly ash	*
9	natural gas	6,42	flue gas	*	*
10	natural gas	5,62	flue gas	*	*
11	fuel oil	13,77	flue gas	fly ash	*

Results and Discussion

1. PCDD/F emissions

Table 2 summarises results related to the three different matrices evaluated, flue gas, fly ash from the gas cleaning systems and some coals entering the power generation stations. They demonstrate very low PCDD/F levels for all matrices considered. Particularly, in the flue gas case, the results ranged between 0,0005 and 0,0099 ng I-TEQ/Nm^3. These findings are far from those found in the air emissions from other processes, such as waste combustion reported in a number of inventories[1,2,3] and below the established limit of 0,1 ng I-TEQ/Nm^3 adopted in the European Directive Council (Directive 2000/76/EC) for waste incineration, which in the absence of a specific standard could be assumed as a guide value. Bearing in mind the previous facts, no clear conclusions can be obtained about the influence of operating conditions because of the low levels determined in all cases.

PCDD/F concentrations associated to the fly ash have varied between 0,48 and 3,00 ng I-TEQ/Kg for power generation stations working with coal and 19,73 ng I-TEQ/kg is the dioxin content for fly ash from the facility using fuel oil. Similar values have been reported in Europe for fly ash from different combustion plants[4,5]. Considering this low PCDD/F content, it is important to point out that the possible reutilization of such ashes would not involve the mobilisation or incorporation of these pollutants to other industrial processes. Dioxin concentrations in the different coals have ranged between 0,23 and 5,29 ng I-TEQ/kg,

2. Typical patterns

Each matrix resulting from the eleven sampling campaigns has been analysed to obtain a comparative study of the different installations.

Figure 1 shows the mean patterns related to flue gas from all the plants evaluated, as a function of type of fuel. In the majority of the cases, the isomer-specific analysis revealed a predominance of Octa- and Hepta-chlorinated congeners. The highest concentration was reached for OCDD, ranging from 2,67 up to 34,49 pg/Nm^3, followed by 1,2,3,4,6,7,8-HpCDD, with values between 1,86 and 30,30 pg/Nm^3. OCDF (3,20 – 49,42 pg/Nm^3) and 1,2,3,4,6,7,8-HpCDF (0,10 – 19,75 pg/Nm^3) were also detected in all samples. The rest of congeners are in a minor proportion or below to the detection limit (LOD). Comparable trends have been published in literature[6]. Patterns are analogous independently on the fuel used. Fly ash samples presented PCDD/F concentration profiles like the corresponding flue gas, with predominance of Octa- and Hepta-chlorinated congeners.

3. Air Emission Factor

The dioxin levels determined in the flue gas were employed to estimate the preliminary air emission factors from the eleven plants. As power generation is the aim of these plants, in the case of the fossil fuel combustion, the PCDD/F amount cannot be easily equated to masses of fuel burned. Consequently and considering the wide variety of fuels used, air emission factors have been expressed in ng I-TEQ/MWh and µg I-TEQ/TJ to reach homogenous data. Table 3 shows the air emission factors estimated from information supplied from the different facilities. Results are similar to those reported for other European countries[7].

Table 2. PCDD/F emissions from eleven Spanish power generation stations evaluated during 2003-2005.

REFERENCE	FLUE GAS (ng I-TEQ/Nm^3)	FLY ASH ng I-TEQ/kg	FUEL ng I-TEQ/kg
1	0,0019	1,18	5,29
2	0,0013	1,40	0,23
3	0,0015	0,83	0,49
4	0,0009	3,00	4,91
5	0,0011	0,59	*
6	0,0093	0,49	0,26
7	0,0044	0,81	0,37
8	0,0099	0,48	*
9	0,0018	*	*
10	0,0026	*	*
11	0,0005	19,73	*

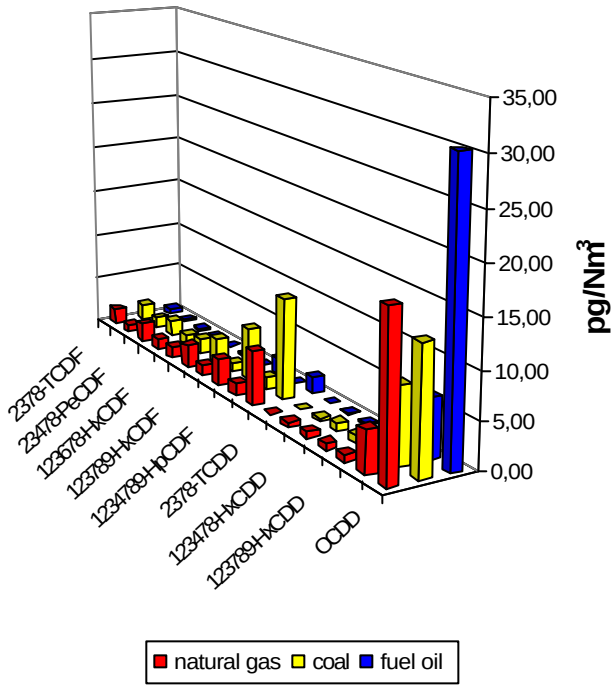

Figure 1. PCDD/F concentration profiles in flue gas related to power generation plants working with different type of fuel.

Table 3. Air emission factors corresponding with all power plants evaluated.

REFERENCE	AIR EMISSION FACTOR ng I-TEQ/MWh	AIR EMISSION FACTOR µg I-TEQ/TJ
1	9,84	2,60
2	8,00	2,22
3	8,72	2,42
4	7,20	2,00
5	5,87	1,63
6	58,99	16,39
7	25,36	7,04
8	37,70	10,47
9	8,55	2,38
10	7,88	2,19
11	1,50	0,42

From these findings and with information from the Spanish power generation sector, both the national emission factor for air releases and the total contribution of this sector in the PCDD/F Spanish inventory will be determined. Additional research considering more experimental measurements could confirm data existing.

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