

## Occurrence Of Pcdds/Fs And Dl-Pcbs In Stationary Gas Emissions From A Waste Management Plant

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### 1. Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/Fs) are two series of chlorinated aromatic compounds formed by a total of 210 compounds divided in 75 PCDDs and 135 PCDFs. Commonly known as dioxins, these substances are markedly anthropogenic and non-intentioned compounds formed as by-products in a variety of industrial processes which include combustion and other chemical reactions such as the production of a number of technical formulations. On the contrary, polychlorinated biphenyls (PCBs) are a family of chlorinated substances composed by a total of 209 compounds. PCBs are man-made products which have been far manufactured in the last decades as a technical formulation for a variety of industrial applications such as flame retardants in electrical transformers or stabilizers in plastic polymers.

In Spain, great efforts and comprehensive studies on combustion processes have been performed over the last years<sup>1,2</sup>. Nevertheless, there is a lack of information on dioxin-like PCBs emitted from stationary gas emissions. Only a few works reported levels of both PCDDs/PCDFs and PCBs from combustion processes<sup>3</sup> and related with other industrial processes<sup>4</sup>.

In this sense, this work presents the findings of both dioxins and dioxin-like PCBs in stationary gas emission samples collected from the stack in a municipal waste management plant. The MWI plant under study is located in Madrid and began its activity in 1995 with a capacity of 1200 Mg per day urban solid waste (USW) plus 300 of non-reusable materials (refuse derived fuel, RDF) from an external waste management. All reusable materials such as paper, plastics, metals and glasses are separated from the bulk and RDF are thermally treated in an advanced revolving fluidized bed process. The thermal process handles approximately 850 Mg per day RDF and produces 29 MW of electricity.

The first layout of the thermal plant presented three identical incineration units equipped by a fluidized bed furnace connected to a semi-dry air pollution control system (APCS) formed by cyclones followed by CaOH absorbers and fabric filters. In addition, the APCS was optimized by the injection of activated carbon.

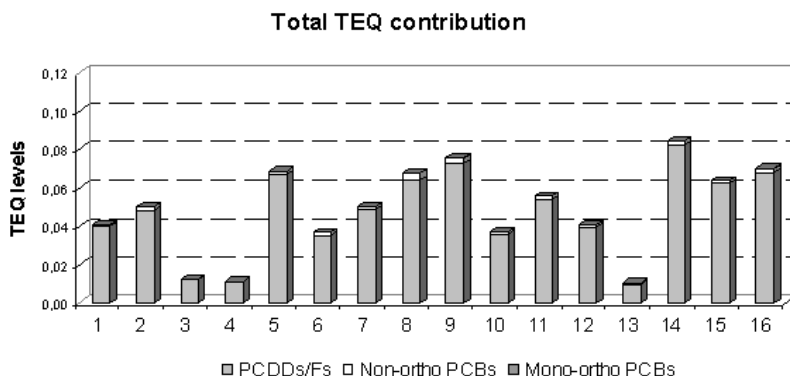
### 2. Materials and Methods

A number of sampling collection episodes were designed during 2004 in order to evaluate the three combustion lines which operates in routine for a period of one year. Sampling was performed following the steps indicated in EN-1948:1996 part 1<sup>5</sup>. Sample solid fraction (XAD-2 and the filter) was Soxhlet extracted with 400 mL toluene as a solvent for 24 h. Prior to the extraction, the solid portion was spiked with a known amount of <sup>13</sup>C<sub>12</sub>- PCDD/PCDFs and <sup>13</sup>C<sub>12</sub>- DL-PCBs mixture (EN-1948-ES and WHO-PCBs LCS). Liquid-liquid extraction was used to extract the target analytes from the condensates using 100 mL dichloromethane in triplicate. The extracts from the three fractions were mixed into one, transferred to n-hexane and rotary-concentrated until 1-2 ml approximately prior to the clean-up process.

Purification was based on solid-liquid adsorption chromatography. The clean-up step was performed by means of an automated system (Power Prep TM, FMS, Inc, MA, USA). The clean-up procedure consists of a sequential array of the three different Teflon prepacked columns: multilayer silica, alumina and PX-21 carbon adsorbents, respectively (FMS Inc, Boston, USA). Analytes were isolated in two different fractions: F1 contained mono-ortho PCBs and F2 contained non-ortho PCBs and PCDDs/PCDFs. Briefly, the extracts were loaded and pumped through individual sets of multilayer silica followed by a basic alumina column with approximately 120 mL of n-hexane. A fraction of the mono-ortho PCBs were eluted from the alumina column with 60 mL n-hexane:dichloromethane (98:2). Next, PCDDs/PCDFs and the rest of DL-PCBs were transferred from the alumina column into the PX-21 carbon column with 120 mL of n-hexane:dichloromethane (1:1) where they remained adsorbed. Meanwhile, a second fraction of mono-ortho PCBs were eluted from carbon and mixed with the previous fraction composing F1. In the carbon column, interferences were removed with a small fraction of ethyl acetate:toluene (1:1) in the forward direction while PCDDs/PCDFs and



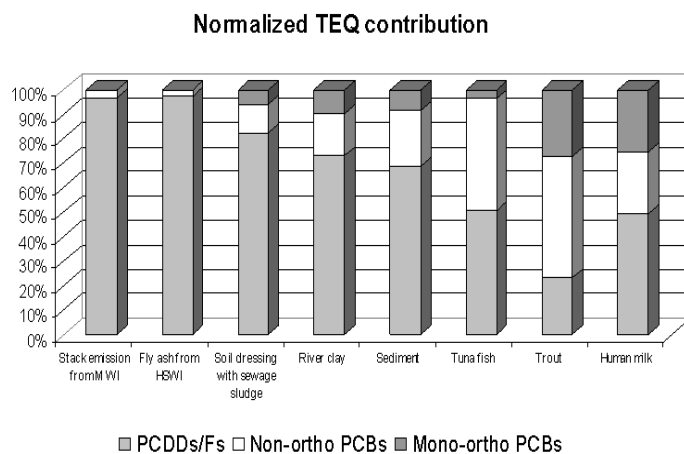
expressed in ng/Nm<sup>3</sup>.



0.1. These findings are in accordance with those reported by other authors<sup>4, 12</sup>. On the contrary low contribution from PCB# 118 was achieved since the TEF was 0.0001 despite of highest concentration determined in all the samples analyzed.

The last part of this study was to compare our findings with different matrices of both environmental and biotic origin. To these purpose relevant samples analyzed in our laboratory (fly ashes from waste incineration, soils dressing with sewage sludge, river clays, sediments, fishes from both fresh and marine water and human milk) included as test materials in several intercalibration exercises<sup>13, 14, 15</sup> were selected for evaluation. Summarized data are given in Figure 3.

Figure 3. Comparison of normalized data of PCDD/PCDF, non-ortho and mono-ortho PCBs in several environmental and biological samples.



where DL-PCBs can contribute to the total TEQ up to 77% for instance in trout samples. Furthermore, important contribution still comes from PCB#126 but not necessarily the highest due to higher concentration determined by the remaining DL-PCBs. Moreover, PCB#118 still presents the highest concentration but in comparison with combustion major proportions of this compound up to 55% for instance in trout can be easily found in environmental or biotic samples.

#### 4. References

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Particular attention was paid on TEQ values. Figure 2 presents the results expressed in TEQ values including both dioxins and DL-PCBs. The findings resulted in a low contribution from DL-PCBs versus PCDDs/Fs. Average contribution to the total TEQ was established in around 3 % including both non-ortho and mono-ortho PCBs. From this fact particular attention to PCB#126 should be derived since this compound contributes with approximately 2-2.5% to the total TEQ because assigned TEF of

In general, as expected similar distributions were achieved when comparing matrices with same origin such as fly ashes from municipal or hazardous waste incineration with a contribution around 3% to the total TEQ from DL-PCBs. Moreover, major contribution comes from non-ortho PCBs mainly from PCB#126 remaining mono-ortho PCBs in a minor proportion. On the contrary, conclusive differences were early reached for both biotic and environmental matrices in which the contribution to the TEQ from DL-PCBs varied depending on the origin. In soils and related samples a contribution nearly 30% can be early reached. Much more remarkable were, however, the differences in biotic samples

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