Polychlorinated dibenzo-\(p\)-dioxins, dibenzofurans and ‘dioxin-like’ PCBs in flue gas emissions from municipal waste management plants

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Abstract

The aim of this work is to give representative data on polychlorinated dibenzo-\(p\)-dioxins (PCDD), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyl (PCBs) from stack gas emissions of an urban solid waste management plant which has to comply with the limit of 0.1 ng I-TEQ/N m\(^3\). In particular, the study is focused on 29 target compounds, the seventeen 2,3,7,8-PCDDs/Fs, four non-ortho PCBs and eight mono-ortho PCBs which configure so-called ‘dioxin-like’ PCBs (DL-PCBs). To this end, emission measurements were performed during one year over the three operating combustion lines in a selected waste management plant. In general, accurate methodology allowed characterizing all target compounds in almost all the samples analyzed. In addition, a typical pattern for DL-PCBs is reported. The pattern presented PCB #118 to be the highest, nevertheless the figures demonstrated DL-PCBs contribution to the total TEQ around 3% being PCB #126 the most important congener due to its TEF of 0.1. Finally, remarkable differences were achieved in comparison with both environmental and biological samples such as soils, sediments, human milk or fish since these matrices may present DL-PCB contribution to the total TEQ up to 77%.

Keywords: PCDDs/Fs; PCBs; Polychlorinated dibenzo-\(p\)-dioxins; Polychlorinated dibenzofurans; Polychlorinated biphenyls; Dioxin-like; Waste management; Combustion

1. Introduction

Polychlorinated dibenzo-\(p\)-dioxins and dibenzofurans (PCDDs/PCFs) 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 (Olie et al., 1977; Rappe, 1994; Fiedler, 1996).

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 as examples (Jensen, 1972).

Both, dioxins and PCBs are characterized by particular physical and chemical properties such as highly stable even in extreme conditions. Moreover, they are lipophilic molecules and might persist in all environmental compartments giving rise to bioaccumulation and consequently biomagnification phenomena. Therefore, they can easily arise up to the top of the trophic chain including humans, being the diet the most important via for an exposition to these toxicants (Jensen et al., 1969; Van Leeuwen et al., 2000).

At present time, these chemicals have been subject of great concern because of their toxicity. There is wide evidence of the adverse effect of chlorinated aromatic compounds with a dioxin-like activity on exposed metabolisms even at very low concentrations (WHO, 1997). For instance, in 1997, the International Agency for Research on Cancer (IARC) declared the 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) to be carcinogenic to humans (WHO, 1997). On the other hand, all PCBs can be considered as toxicants but the most hazardous are those identified by the World Health Organization (WHO) as ‘dioxin-like’ PCBs, a group of 12 PCBs which has been includes 4 non-ortho and 8 mono-ortho PCBs. Because of their structural similarity with dioxin and their toxicological behavior a toxic equivalence factor (TEF) referred to the toxicity of the 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) have been assigned (Van den Berg et al., 1998).

As a consequence, a number of measures to protect and improve the quality of human health are being enforced world wide. In particular, in 1996, the EU member countries adopted limits for PCDD/PCDF from stationary gas emissions of 0.1 ng I-TEQ/N m$^3$ (Council Directive 2000/76/EC). Other actions relate to the maximum concentration of these pollutants in food for human consumption and feed for animal nutrition (Council Directive 2001/102/EC, 2002; Council Regulation EC No. 2375/2001, 2001).

In connection with this, monitoring plays an important role in public and sanitary decisions. However, representative data requires the use of appropriate methods and procedures. Since Jensen in 1969 (Jensen et al., 1969; Jensen, 1972) and Olie in 1977 (Olie et al., 1977) great efforts and developments have been performed to obtain a reliable procedure for an accurate determination dioxin and ‘dioxin-like’ PCBs and a number of analytical methodologies derived from well recognized official methods were developed for quantitative analysis of the 17 toxic 2,3,7,8-chlorine substituted PCDD/Fs and 12 DL-PCBs (EPA 1613, Method 1613, 1995; EN-1948-1,2,3:1996; EPA1668, Method 1668, 1999). The analysis of PCDD/Fs and DL-PCBs is usually carried out by high resolution gas chromatography coupled to high resolution mass spectrometry (HRGC–HRMS) operating above 10000 of mass resolution and using the isotope dilution as a quantitative method. Magnetic sector instruments provide the required specificity and sensitivity for organic traces.

Nevertheless, with independence of the MS method, an efficient cleanup is unavoidable prior to HRGC–HRMS analysis. Classical methods described in official methods are based on the solid–liquid adsorption chromatography in open columns using different adsorbents. The main drawbacks of these methods are that these systems are time-consuming and require manual sample manipulation (Focant et al., 2004). At present, several authors reported data describing automated systems which allow processing unattended samples in a relative short time (Abad et al., 2000; Pirard et al., 2002; Focant et al., 2004). Moreover, the development of new phases for a specific GC separation (Cochran and Frame, 1999; Santos and Gakerman, 2002, 2003), the synthesis of new labeled standards or the study of a number of MS techniques as alternative constitute new challenge in the analysis of these toxicants (Santos et al., 2003, 2004). In addition, bioassays appear to be complementary procedure to well-defined chemical methods for screening in the study of these toxicants in feed and food (Behnisch and Hoogenboom, 2004).

In Spain, great efforts and comprehensive studies on combustion processes have been performed over the last years. Firstly, waste management was extensively studied giving rise a number of works which report temporal trends on thermal processes in consonance with new environmental standards (Abad et al., 1997a, 2002, 2003). Therefore, a dioxin inventory from municipal waste incineration sector was performed (Fabrellas et al., 2001). In addition, dioxin emissions from coal-fired power stations were also evaluated (Fernández-Martinez et al., 2004). Recently, dioxins were characterized in emission from cement kiln plants. Moreover, the influence of using waste materials, such as tires or meat meal, as secondary fuel during clinker production on the PCDD/F emission levels were evaluated (Abad et al., 2004).

Despite the number of studies reported data about total TEQ including dioxins and dioxin-like PCBs in a variety of food and biological matrices, there is a lack information on dioxin-like PCBs emitted from stationary gas emissions. Only a few articles reported levels of both PCDDs/PCDFs and DL-PCBs from combustion processes. Gardinali et al. describe accurate methodology for the analysis of mono-ortho, di-ortho and non-ortho PCBs and PCDDs/PCDFs in environmental samples (Gardinali et al., 1996). In the same way, interesting data was described by Aries et al., which reported a developed method for analysis of ’dioxin-like’ PCBs in environmental samples from the steel industry is particularly described (Aries et al., 2004). In addition, congener distri-
bution of both PCDDs/PCDFs and DL-PCBs is given. Finally, the authors summarized that analysis of a waste dust sample from UK sinter showed a relatively low concentration of DL-PCBs when comparing it to the toxic load of PCDDs/PCDFs. Luthardt et al. reported levels and distribution of PCDDs/PCDFs and DL-PCBs from industrial sources such as waste management plants, cement kilns, sinter plants and crematories. Dioxin-like substances were detected in all samples analyzed and slight differences in DL-PCBs contribution were achieved with values up to 20% (Luthardt et al., 2002).

In this sense, this paper 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

2.1. Chemical reagents and standard solutions

All solvents (acetone, dichloromethane, toluene, ethyl acetate, n-hexane and isooctane) for organic trace analysis were purchased from Merck (Darmstadt, Germany). Nonane and tetradeccane were from Fluka (Fluka chemie GmH. Switzerland). Amberlite XAD-2 was obtained from Supelco (Supelco, Bellefonte PA, USA). Glass fiber filters were from Whatman (Whatman International Ltd., Maidstone, England). Multilayer silica, basic alumina and activated carbon were obtained from FMS Inc. (FMS Inc., Boston, USA). Perfluorokeronese (PFK) low boiling grade for mass spectrometry was fromSigma Aldrich (Spain). Quantification of 2,3,7,8-PCDDs/PCBs and DL-PCBs were performed following minimum requirements described in EN-1948:1996 and EPA method 1668A. For this purposes standard solutions in nonane (EN-1948 CS-1 to CS-6, EN-1948 ES, EN-1948 SS, EN-1948 IS, WP-LCS, WP-ISS, WP CS-1 to WP CS-7 from Wellington Labs., Guelph, Ontario, Canada) were used for instrument calibration, quantification, sampling and analytical recovery. Certified reference materials (CRM 490, 1996; CRM 615, 2002) were also purchased from Wellington Laboratories quality assurance and quality control (QA/QC).

2.2. Sampling

The purpose of this work is to study the dioxin and dioxin-like PCBs presence and distribution in stack gas emissions released to the atmosphere from a municipal waste management plants which apply a thermal process in a residual waste (RDF) after treatment of raw urban solid waste (USW). To this aim, a number of sampling collection episodes were designed in order to evaluate the three combustion lines which operates in routine for a period of 1 year.

Sampling was performed following the steps indicated in EN-1948:1996 part 1 using a filter/condenser device as a sampling train. The filter was placed after the probe. The gas temperature in probe and filter was regulated at 120°C. XAD-2 (Merck, Germany), previously cleaned, was used as an adsorbent trap. During the sampling process, the resin was cooled at 20°C by re-circulated water. Thus, approximately 10 cubic meters sample in normal conditions (N m³) were collected from the stack for a period between 6 and 8 h. The process was controlled by putting 100 μl work standard solution EN-1948 SS composed by three PCDFs in concentrations of 4 pg/μl for penta- and hexa- and 8 pg/μl for heptachlorinated congeners in nonane (4% tetradecane as a keeper).

2.3. Extraction and clean up

Once collected, the samples were sent to the laboratory to continue with the analysis. Briefly, stack gas samples are formed by a solid fraction composed by 30 g amberlite XAD-2 and the filter; a second fraction consisted in an aqueous solution from the combustion reaction. Moreover, all parts of the sampling train in contact with the sample were rinsed with two solvents, first with acetone followed by toluene. This could be assumed as a third fraction.

Solid fraction 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 13C12-PCDD/PCDFs and 13C12-DL-PCBs mixture (EN-1948-ES and WHO-PCBs LCS). Liquid–liquid extraction was used to remove analytes from the aqueous portion using 100 ml dichloromethane in triplicate. The extracts from the three fractions were mixed into one and then transferred to n-hexane and rotary-concentrated. The organic extract was concentrated in a rotary evaporator (Büchi, Switzerland) until 1–2 ml approximately prior to the clean-up process. Before clean up, the resulting extract was then filtered through a 1 μm PTFE filter to a tube.
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 pre-packed columns: multilayer silica, alumina and PX-21 carbon adsorbents, respectively (FMS Inc., Boston, USA). In our scheme, fractionation is achieved with a solvent sequence and thus, analytes were isolated in two different fractions. First fraction (F1) contained mono-ortho PCBs and a second fraction containing 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 portion of mono-ortho PCBs were collected with 60 ml n-hexane: dichloromethane (98:2). Next, PCDDs/PCDFs and DL-PCBs were eluted from the alumina column and transferred to the PX-21 carbon column with 120 ml of n-hexane:dichloromethane (1:1) where they remained adsorbed. Meanwhile, a second portion of mono-ortho PCBs were substantially eluted and mixed with previous fraction composing F1. In carbon, interferences were eluted with a small fraction of ethyl acetate:toluene (1:1) in the forward direction, and PCDDs/PCDFs and non-ortho PCBs were collected from the carbon column in the reverse direction with toluene forming F2 fraction (Eljarrat et al., 2002; Pirard et al., 2002).

Finally, the extracts were rotary concentrated and put into a vial. Then, the remaining solvent was reduced to dryness by a gentle stream of nitrogen. Final extracts from F1 (mono-ortho PCBs fraction) were reconstructed to 10 μl by adding a known amount of syringe working formed by a mixture of labeled PCBs (WHO-PCBs ISS). In addition, F2 extracts (PCDDs/PCDFs and non-ortho PCBs) were reconstructed to 30 μl by adding a known amount of syringe standard for both kind of analytes.

2.4. HRGC–HRMS analysis

Instrumental analysis was based on the use of high resolution gas chromatography coupled to high resolution mass spectrometry (HRGC–HRMS). All analyses were performed on a Agilent gas chromatograph fitted with a high resolution 40 m × 0.18 mm i.d. × 0.18 μm film thickness DB-5 ms fused silica column (J&W Scientific, CA, USA) connected through a heated transfer line kept at 280 °C to a Micromass Ultima NT high resolution mass spectrometer (EBE geometry) controlled by a Masslynx data system. All sample injections, as solutions in nonane, were carried out by a PAL system under data control system. The injector port temperature was 280 °C, and a helium carrier gas flow was maintained by an electronic pressure program. The GC capillary temperature program for fractions was as follows: initial 140 °C (hold for 1 min), then at 20 °C/min to 200 °C and kept isothermally for 1 min and at 5 °C/min to 310 °C (hold for 6 min). Analytes were separately analyzed in three different acquisitions, one for PCDDs/PCDFs, a second for non-ortho PCBs and a third fraction for mono-ortho PCBs. As a confirmatory purposes a GC capillary column 50 m × 0.25 mm i.d. × 0.25 μm film thickness CP-SIL88 fused silica column (Chrompack, The Netherlands) was employed when required. In this case the temperature program was as follows: 140 °C (1 min) to 200 °C (1 rain) at 15 °C/min then at 2 °C/min to 200 °C, then at 2 °C/min to 240 °C and hold isothermally for 40 min at 240 °C (Abad et al., 1997b).

Chromatograms of GC effluents were achieved using a positive electron ionization (EI+) source and operating in the SIM mode at approximately 10000 resolving power (10% valley definition). The two most abundant ions in the [M Cl]+ cluster were monitored with equal dwell time and delay time of 50 ms and 20 ms respectively. The ion source temperature was kept at 250 °C; at an electron beam current of 600 μA, and ion acceleration voltage of 8 kV. The electron beam energy was adjusted to maximize the response for the m/z 331 ion of PFK.

Quantification was carried out by the isotopic dilution method. Relative response factors were performed for each individual analyte by the analysis of six different calibration solutions for PCDDs/PCDFs and seven in the case of DL-PCBs. The results are expressed TEQ values using both, I-TEF and WHO-TEF (NATO/CCMS, 1988; Van den Berg et al., 1998). TEQs values were calculated in lowerbound assuming zero for those non-quantifiable or below the limit of detection (LOD). The detection limit for PCDD/PCDF is defined as the minimum concentration of analyte that produces a clear peak with an acceptable chlorine isotope ratio and with a signal-to-noise ratio equal to 3. In our study, the chlorine isotope ratio for the molecular cluster ions was within ±15% of the theoretical ratio and the peak responses for each of the two selected molecular cluster ions were at least three times the background noise level.

2.5. Quality criteria

The criteria for ensuring the quality data include the application of the quality assurance and quality control (QA/QC) measures. A survey of laboratory cross-contamination showed that after the analysis of a series of control blanks, monthly performed and covering whole methodology the average contribution to the total TEQ did not exceed in 0.5%. In addition, field blanks including sampling episode and shipment to the laboratory were strategically carried out along the study. In the majority of the cases, the analytes keep below limit of detection or not detected and only traces of highly chlorinated compounds were quantified. Other internal and routinely checks performed consider aspects such as sensitivity and power resolution of mass spectrometer,
accurate GC separation and retention times, correct isotopic ratio or acceptable recovery rates.

The trueness of the data was also contrasted by analyzing related certified reference materials (CRM) such as CRM 490 or CRM 615, both fly ashes certified for PCDDs/PCDFs (CRM 490, 1996; CRM 615, 2002). Complementarily, the successfully participation in recognized intercalibration exercises constituted an excellent tool to evaluated generated data. Thus, DL-PCB performance was achieved from the intercalibration exercises since no related materials were available for that kind of compounds (Van Bavel et al., 1996, 1998; Becher et al., 2004). The participation in the last eight intercalibration exercises organized by Professor Bert van Bavel from the University of Orebro (Sweden) demonstrated in all cases good correlation within consensus with $Z$ score $\pm 2$.

### 3. Results and discussion

The goal of this work was to assess the presence of PCDDs/Fs and DL-PCBs in stack gas emission from a municipal waste management plant. To this purpose, a series of sampling campaigns were designed and performed along 2004 in a selected plant placed in Madrid.

<table>
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<th>Maximum</th>
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<th>LOD (%)</th>
<th>Average $R$</th>
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<td>PCB #114</td>
<td>6.78</td>
<td>5.65</td>
<td>1.31</td>
<td>15.17</td>
<td>4.20</td>
<td>62</td>
<td>0.510</td>
<td>88</td>
<td>Internal standard</td>
</tr>
<tr>
<td>PCB #118</td>
<td>41.90</td>
<td>35.57</td>
<td>17.34</td>
<td>132.48</td>
<td>27.02</td>
<td>64</td>
<td>0.490</td>
<td>90</td>
<td>Internal standard</td>
</tr>
<tr>
<td>PCB #123</td>
<td>4.17</td>
<td>4.05</td>
<td>1.29</td>
<td>8.57</td>
<td>2.10</td>
<td>50</td>
<td>0.539</td>
<td>90</td>
<td>Internal standard</td>
</tr>
<tr>
<td>PCB #156</td>
<td>13.22</td>
<td>12.26</td>
<td>4.60</td>
<td>29.77</td>
<td>6.58</td>
<td>50</td>
<td>0.395</td>
<td>84</td>
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</tr>
<tr>
<td>PCB #157</td>
<td>10.70</td>
<td>10.45</td>
<td>2.12</td>
<td>23.80</td>
<td>5.71</td>
<td>53</td>
<td>0.392</td>
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</tr>
<tr>
<td>PCB #167</td>
<td>6.18</td>
<td>5.43</td>
<td>1.93</td>
<td>11.52</td>
<td>2.77</td>
<td>45</td>
<td>0.410</td>
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</tr>
<tr>
<td>PCB #189</td>
<td>16.15</td>
<td>15.88</td>
<td>2.53</td>
<td>43.59</td>
<td>10.27</td>
<td>64</td>
<td>0.379</td>
<td>84</td>
<td>Internal standard</td>
</tr>
<tr>
<td>TEQ (including DL-PCBs)</td>
<td>48.34</td>
<td>50.04</td>
<td>10.27</td>
<td>84.37</td>
<td>23.14</td>
<td>48</td>
<td></td>
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</tr>
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</table>
in order to collect representative samples from the three operating combustion lines.

Once collected, samples were shipped to the laboratory to continue the analysis. The entire methodology previously described was applied to determine PCDD/F and DL-PCB contents in flue gas emissions. Congener-specific analyses were successfully accomplished over 16 samples. This allowed characterizing distribution in such matrices of 29 target analytes, the 17 well-known 2,3,7,8-chlorosubstituted PCDDs/Fs and 12 DL-PCBs (PCBs #77, #81, #126, #169, #105, #114, #118, #123, #156, #157, #167 and #189, PCBs numbering in agreement with reported by Ballschmiter and Zell) (Ballschmiter and Zell, 1980).

Raw data including concentrations, TEQ values, limit of detection and recovery rates are summarized in Table 1. As expected for a new plant equipped with a modern APCS overall data revealed dioxin emission concentrations below 0.1 ng I-TEQ/N m$^3$ ranging between 0.01 and 0.08 ng I-TEQ/N m$^3$ with an average and a median of 0.047 and 0.048 ng I-TEQ/N m$^3$, respectively. Limit of detection varied between 0.103 for tetrachlorinated to 1.38 pg/N m$^3$ for octachlorinated congeners. These values are in agreement with the values described in previous experiences such as reported in EN-1948 (EN-1948, 1996). Moreover, PCDD/F presented a classical combustion pattern extensively reported in the literature (Abad et al., 1997a,b). In addition, in Figs. 1 and 2 are given a typical dioxin distribution in both concentration and TEQ comparable to those reported in previous works (Abad et al., 2002).

Interesting data was observed for PCBs. In agreement with previous data documented in the literature, the 12 DL-PCBs were detected, assigned and quantified in almost all the samples analyzed. Comparable values of LOD were also obtained for DL-PCBs with values

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**Fig. 1.** PCDD/PCDF and DL-PCB congener profile in stack gas emission samples from a municipal waste management plant expressed in pg/N m$^3$. 
ranging from 0.138 to 0.539 pg/N m$^3$. Figs. 3 and 4 exemplifies achieved chromatograms of both, non-ortho and mono-ortho PCBs, respectively. Remarkable differences might be found in the samples according to the concentrations, the compounds or the combustion conditions, but as a first approach the levels ranged from 1 to 132 pg/N m$^3$. Nevertheless, large similarities were found between the samples, independently of the combustion unit assessed and a particular behavior was repeatedly observed for this kind of combustion matrices. In general, DL-PCBs concentrations contributed to the total 'dioxin-like' compounds quantified in this study with an average of 14% and a median of 12% (Fig. 5). This means that major concentration of ‘dioxin-like’ substances emitted to the atmosphere comes from PCDDs/PCDFs instead of DL-PCBs which is in accordance with previous data reported by Aries et al. in steel related matrices (Aries et al., 2004). In addition, in all cases higher concentration of mono-ortho PCBs was determined in comparison to non-ortho PCBs with concentrations of mono-ortho PCBs up to four fold higher compare to non-ortho. In particular, highest concentration was determined for PCB #118 (also considered as marker PCB) with a contribution varying between 12% and 46% with a mean value and a median of 26% and 22% respectively, the remaining eleven compounds contributing in a minor proportion. To illustrate this fact, individual normalized distribution of all of the 29 target substances in emission samples for each individual measure expressed in concentration (pg/N m$^3$) is given in Fig. 6.

Particular attention was paid on TEQ values. Fig. 5 presents individual 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

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**Fig. 3.** Non-ortho PCB pattern in stack gas emission samples from a municipal waste management plant.

**Fig. 4.** Mono-ortho PCB pattern in stack gas emission samples from a municipal waste management plant.
total TEQ because assigned TEF of 0.1. These findings are in accordance with those reported by other authors (Aries et al., 2004; Luthardt et al., 2002). 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 differences to the total TEQ achieved by using I-TEF or WHO-TEF in this type of matrices were also assessed. In our experience, an increase of slight difference was observed total TEQ ratios, $P(\text{WHO-TEF}_i / \Sigma \text{conc. 2,3,7,8-PCDDs/PCDFs}_i) / P(\text{I-TEF}_i / \Sigma \text{conc. 2,3,7,8-PCDDs/PCDFs}_i)$, were about 1.03 which means an increase of 2.6% in total TEQ, when DL-PCBs are not included. On the other hand, the inclusion of DL-PCBs and calculating total TEQ by using WHO-TEF would mean $P(\Sigma (\text{WHO-TEF}_i / \Sigma \text{conc. 2,3,7,8-PCDDs/PCDFs}_i) + \text{WHO-TEF}_i / \Sigma \text{conc. DL-PCBs}_i) / \Sigma ((\text{I-TEF}_i / \Sigma \text{conc. 2,3,7,8-PCDDs/PCDFs}_i) + \text{WHO-TEF}_i / \Sigma \text{conc. DL-PCBs}_i)$ of 1.06 which would mean an increase of total TEQ about 6%. Furthermore, no differences were observed when quantifying following upperbound, mediumbound or lowerbound criteria because all compounds were above the limit of detection in almost in all cases studied.

At present, it is also recognized that dioxin fingerprint analysis constitutes an excellent tool to link a particular source with the potential impact to the environment. In addition, it is extensively documented existing specific dioxin fingerprint derived from a particular source, process or matrix. The last part of this study was to compare our findings to other 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 (Van Bavel et al., 1996, 1998; Becher et al., 2004) were selected for evaluation. Summarized data are given in Fig. 7.

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

**Fig. 5.** TEQ data of PCDD/PCDF and DL-PCBs in stack gas emission samples from a municipal waste management plant expressed in ng/N m$^3$.

**Fig. 6.** Normalized data of PCDD/PCDF, non-ortho and mono-ortho PCBs in stack gas emission samples from a municipal waste management plant expressed in pg/N m$^3$. 
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 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.

References


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