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Long-time monitoring of polychlorinated dibenzo-p-dioxins and dibenzofurans over a decade in the ambient air of Porto, Portugal

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HIGHLIGHTS

- A trend of PCDD/PCDF levels in ambient air over thirteen years was studied.
- A decrease on PCDD/PCDF concentrations was found.
- Seasonal variations and possible sources of the PCDD/PCDF were assessed.
- Homologue and congener profiles over the years of study were characterized and discussed.

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ABSTRACT

As part of a monitoring program initiated in 1998 and conducted by IDAD – Institute for Environment and Development and supported by regional municipal solid waste (MSW) management authorities, an extensive database of dioxins' and furans' (PCDD/PCDF) concentrations in ambient air was collected in Porto, in two sites classified as suburban. The present paper summarizes the analytical results of PCDD/PCDF in ambient air obtained from 2001 to 2014 through this intensive monitoring work. The toxic equivalent (WHO-TEQ 1998) concentrations of the PCDD/PCDF in the air ranged from 8.2 to 904.4 fg TEQ m^{-3}, with an average and median values of 104.5 fg TEQ m^{-3} and 49.8 fg TEQ m^{-3}, respectively. The PCDD/PCDF concentration trend in Porto's ambient air shows a clear drop of the annual average values occurred during the study period. The presence of seasonal variations is very clear in the present study. Winter levels (average: 154.3 fg TEQ m^{-3}) are significantly higher than summer levels (average: 42.9 fg TEQ m^{-3}). The PCDD/PCDF profiles' details show that several differences occurred over time. The homologue profiles presented changes and the PCDD congeners have decreased in terms of mass. The analysis of concentrations in combination with specific homologue and congener patterns of PCDD/PCDF allowed identification of potential emission sources.

1. Introduction

The polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF), often simply termed as dioxins, are unwanted by-products of the synthesis and combustion of chlorinated organic chemicals. Due to these properties PCDD/PCDF are considered highly toxic compounds that belong to the group of persistent organic pollutants (POPs), defined by the Stockholm Convention on Persistent Organic Pollutants in 2001.

Special attention has been paid to these substances taking into account their toxicity, environmental persistence, and capacity for bioaccumulation. According to the European Environmental Agency (EEA) the exposure to normal background levels of PCDD/PCDF is unlikely to cause health problems, although some PCDD and PCDF may cause cancer and may affect the unborn children even in exposures of low concentrations (EEA, 2013). The human exposure to these chlorinated contaminants occurs mainly via food consumption, and more specifically, the ingestion of fatty foodstuffs (Llobet et al., 2008).

The ambient air PCDD/PCDF concentrations can vary widely depending on the type of area investigated and on the presence of different emission sources, such as combustion activities (e.g., municipal waste incineration, hospital waste incineration, wood burning, forest fires), vehicle exhaust, metal smelting and processing sources, chemical manufacturing, biological and photochemical processes, and reservoir sources (soils, sediments, and treated wood) (O'Keefe et al., 1994; Kjeller and Rappe, 1995; Caserini

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and Monguzzi, 2002; McKay, 2002; Gullett and Touati, 2003; Lee et al., 2004; Tame et al., 2007; Hsu et al., 2011; Li et al., 2012). After the PCDD/PCDF release into the atmosphere the compounds are dispersed throughout the environment matrices (e.g., soil and/or waters) by atmospheric transport.

During the 1970s and the 1980s, municipal solid waste incineration (MSWI) accounted for the main world-wide contribution of PCDD/PCDF emission (Olie et al., 1998). Currently, semi-dry lime scrubbing and bag filters coupled with activated carbon injection have been playing an important role in the prevention or minimization of PCDD/PCDF in stack gas emission to the environment (McKay, 2002). In addition, after the regulatory limit of 0.1 ng TEQ N m^{-3} entered into force, MSWI is no longer a significant source of PCDD/PCDF.

After global agreements to minimize PCDD/PCDF emissions and introduction of strict emission limits for European industries during the last decade, the industrial facilities have reduced emission of these compounds and the success of these controls can be seen in published time trends (Augusto et al., 2014; Bruckmann et al., 2013; Directive 2000/76/EC, 2000). According to EEA (2013) between 1990 and 2011, PCDD/PCDF emissions dropped in the EU-27 by 85%. In Portugal, a 25% drop in emissions from 2000 to 2011 was estimated (APA, 2013). The introduction of strict emission limits for European waste incineration plants and for industrial installations (Directive 2000/76/EC, 2000) have been demonstrated to be effective in the reductions of PCDD/PCDF emissions (Bruckmann et al., 2013).

Temporal trend data of concentrations in ambient air are an important key to measure the effectiveness of source reduction measures and regulatory controls. Trends of PCDD/PCDF in ambient air have been studied in several countries in different type of sites. One of the longest time series in European's ambient air began in 1991 at six sites in the UK (3 urban, 3 rural/semirural sites) (Katsoyiannis et al., 2010). This trend presented an annually averaged urban concentration typically of 100 fg TEQ m^{-3} in the early 1990s and <50 fg m^{-3} in the mid-2000s (Katsoyiannis et al., 2010). Abad et al. (2007) published the PCDD/PCDF concentration trend of Catalonian (Spain) in ambient air and showed a decline of about 70% from 1997–1998 to 2003–2004. This drop was associated with the use of more efficient gas cleaning systems and linked to a greater concern for environmental protection amongst population in general as well as to the efforts made to reduce the PCDD/PCDF emissions from primary sources (Abad et al., 2007).

The quantification and ranking of the primary sources of PCDD/PCDF emissions in a determined region or zone of the environment is a complex process. However, the details of PCDD/PCDF air concentration profiles can show several differences, which can provide interesting information (Lohmann and Jones, 1998; Alcock et al., 2001). The profiles of PCDD/PCDF are often referred to as "fingerprint" or "signature". Thus, fingerprinting of PCDD/PCDF has been extensively used in source identification.

2. Description of the project

The Metropolitan area of Porto corresponds to 2% (2042 km^2) of the Portuguese territorial area with around 1.7 million citizens that correspond to 17% of the Portuguese population.

In accordance with the municipal solid waste (MSW) management plan adopted for Porto, Portugal, a MSW incinerator with the capacity of 400,000 tons per year (commonly referred to as LIPOR II) was constructed in 1998 (see location in Fig. 1). An ambient air monitoring program for the MSW incinerator in the region of Porto was designed, in order to evaluate the effects of the operation of this facility on the surrounding area (Coutinho et al., 1998). This monitoring program is currently operating.

Since the beginning of the monitoring program in 1998 until the end of 2014 a total of 193 ambient air samples of PCDD/PCDF were collected in different sites in the vicinity of the MSW incinerator providing an extensive characterization of the atmospheric levels of these pollutants in the metropolitan area of Porto, as well as information about the temporal trend of the atmospheric concentration of these compounds. At the beginning of the program, sampling of ambient air for PCDD/PCDF analysis was performed at six different sites; since 2001 regular monitoring was restricted to two sites.

A study published by Coutinho et al. (2006) showed that the shutdown of two medical waste incinerators in Porto in January 2001 caused a sharp decrease in concentrations of PCDD/PCDF of about 50% in both the winter and the summer months. This effect was noticed not only in the total concentration of these compounds, but also on the homologue and congener pattern of the samples.

As a consequence of this pattern change, only data collected after January 2001 are used in the current paper. Thus, the present paper focuses on the description and interpretation of PCDD/PCDF ambient air data obtained in Porto between February 2001 and October 2014, in two different sites, Leça do Balio and V.N. Telha. The considered sites are located approximately 3 km around the incineration plant LIPOR II, on the outskirts of Porto, in areas with suburban characteristics. A total of 143 samples, collected from the two different sites, were available for this study.

3. Materials and methods

3.1. Sampling and analytical method

The sampling apparatus for PCDD/PCDF in ambient air was carried out according to the German guideline VDI 3498 Part 2, 2002. The sampling apparatus consisted of a filter system, a mast, a suction pump, a gas volumeter and a timer. Particulate matter in the air was collected on a glass fiber filter. Filterpassing matter was collected on a polyurethane foam (PUF) absorption filter. To monitor the effectiveness of sampling, a second polyurethane foam sampling unit was connected downstream. The reference volume is the volume of air that is drawn through the sampling device and measured with a gas volumeter during the sampling period (72 h).

The PCDD/PCDF samples which were deposited on the glass fiber filter and absorbed in the PUF, were extracted and cleaned up from interfering components in a multistage separation process. Then they were quantified by gas chromatography/mass spectrometry (HRMS), according to EN 1948.

3.2. Data analysis

In order to provide quality assurance of concentration data, for those congeners with concentration values below the quantification limit (LOQ), it was assumed values corresponding to half the limit of quantification (LOQ).

The congeners analyzed in the monitoring program of Porto are the 7 PCDD and the 10 PCDF that are substituted at 2,3,7,8-positions. They are given a toxicity equivalence factor (TEF) relative to the toxicity of 2,3,7,8-TCDD (TEF = 1). The toxic equivalence factors authorized by the World Health Organization (WHO) in 1998 were used for the calculations of the concentrations of individual congeners or of their sum ($\sum$TEQ), and the results are given as fg TEQ m^{-3} of air. The World Health Organization published new TEF values in 2006, with some minor changes (Van den Berg et al., 2006) from the 1998 version. However, in the present study 1998 WHO–TEF were used in order