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# Long-term monitoring programme of polychlorinated dioxins and polychlorinated furans in ambient air of Catalonia, Spain (1994–2015)

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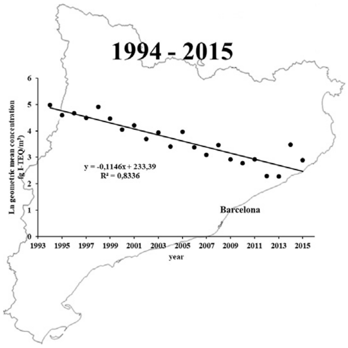
## HIGHLIGHTS

- 22-yr long-term air-monitoring in Catalonia, Spain indicated a decrease in concentrations of PCDD/F.
- Decreasing levels of PCDD/F concentrations were observed at a rate of 11% $yr^{-1}$.
- Winter concentrations were higher with greater variation than summer levels.
- Less chlorinated PCDD/F congeners identified locations with local combustion sources.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Reductions in concentrations of persistent organic pollutants were observed for polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in a comparison of two consecutive decades ending in December 31, 2015 ($n = 413$) and compiled from a 48-station long-term air-monitoring network in Catalonia, Spain. Reductions were observed in geometric mean concentration of total PCDD/Fs, decreasing at a rate of 11% $yr^{-1}$. Results reflect the relative success of improved pollution control measures at industry and traffic locations. At traffic and industrial locations, PCDD/Fs were reduced by around 68% (from 70 to 22 fg I-TEQ/$m^3$) and 66% (from 57 to 19 fg I-TEQ/$m^3$), respectively. The highest concentration of 1196 fg I-TEQ/$m^3$ was observed during the first decade at an industrial location. The highest concentration over the second decade was at a background location during winter (674 fg I-TEQ/$m^3$). Winter observations are generally higher than those recorded in summer, as evident in an 8-year period of moderate PCDD/F levels (<250 fg I-TEQ/$m^3$, $n = 143$). PCDD/F congener profiles were identified has having less chlorinated PCDD/F, indicating the presence of nearby combustion sources at selected locations. More long-term sampling campaigns, combined with network optimization and integration into a meteorological model, can offer a tool for future PCDD/Fs control measures in not only Catalonia – but also applicable to other areas.

## 1. Introduction

Levels of persistent organic pollutants (POPs) in air have become a major human health concern due to their toxicity, bioaccumulation, mutagenicity, carcinogenicity, persistence and global distribution

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(Bostrom et al., 2002; UNEP, 2001). Special attention has been payed to the polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF). These compounds have been reported to be toxic to exposed organisms (IARC, 1997; IARC, 2012). PCDD/Fs are listed in annex C of the Stockholm Convention on POPs (UNEP, 2001) and they are still emitted unintentionally from numerous sources as by products from combustion activities (e.g., municipal waste incineration, hospital waste incineration, wood burning, forest fires), vehicle exhaust, metal smelting and processing sources, biological and photochemical processes, and reservoir sources (soils, sediments, and treated wood) (Coutinho et al., 2015, Abad et al., 2004, Kulkarni et al., 2008).

Ambient air is considered one of two core media targeted to measure PCDDs and PCDFs under the Stockholm Convention (UNEP, 2001; Schuster et al., 2015). Air monitoring data for PCDDs and PCDFs are available from the Global Monitoring Plan of the Stockholm Convention and from National Air Pollution Networks. Air monitoring programmes have provided a basis for tracking dioxins in the environment. Sampling campaigns over time can give important information on changing magnitude of local sources (Lorber et al., 2013). Different studies, with the objective to evaluate the presence and trends of PCDD/Fs in ambient air have been undertaken within the last years. Katsoyiannis et al. (2010) reported levels of PCDD/F in ambient air in UK (3 urban and 3 rural/semirural sites) in a surveillance programme started in 1991 (Katsoyiannis et al., 2010). The authors reported an annually averaged concentration for urban sites of 100 fg International Toxic Equivalents (I-TEQ)/m$^3$ in the early 1990s and <50 fg/m$^3$ in the mid-2000s with a decline of about 87%. A similar trend was observed in a 17 years follow-up study of PCDD/F concentration in ambient air in Porto (Portugal) (Coutinho et al., 2015). In both works, this drop was associated to a decrease of other specific sources of PCDD/F, which are not reported in the emission inventory, and to the larger decrease of emissions due to the use of more efficient gas cleaning systems (Katsoyiannis et al., 2010; Coutinho et al., 2015).

Catalonia (Spain) started a consistent programme for monitoring PCDD/Fs in ambient air in 1994, coordinated by the Environmental Department (Departament de Medi Ambient) of the Catalonian Government (Generalitat de Catalunya) in collaboration with the Dioxin Laboratory (Environmental Chemistry Dept., Institute of Environmental Assessment and Water Research (IDÆA)) of the Spanish Council for Scientific Research (CSIC). The study covers a total area of 1755 km$^2$, with a population of 3,999,268 inhabitants and a population density distribution of 3232 inhabitants/km$^2$ (Institut d'estadística de Catalunya, 2018). To our knowledge, this study represents one of the longest consecutive air monitoring study on dioxins and furans ever conducted in Spain, with a twenty-two-year follow-up period (1994–2015). The aim of this work was to determine PCDD/F levels and to assess temporal trends of the atmospheric content of these pollutants all over Catalonia.

## 2. Materials and methods

### 2.1. Sampling

The main objective was to get representative data from a wide number of sites potentially affected by a number of anthropogenic sources such as industrial activities or traffic exhausts. Also, non-affected areas were subject of study. Thus, data from the analysis of 182 samples, collected in 30 different locations all over Catalonia from 1994 to 2004 have been reported in previous works (Abad et al., 1997a, 1997b, 2001, 2004, 2007). In the present work, results of 231 new samples are showed, collected through the services of the Department of the Environment, from 28 sampling points located in Catalonia for the period of 2005 to 2015. Old locations were re-evaluated, new locations were added, and sampling was chosen to document temporal trends. In summary, from 1994 to 2015, the study design incorporated a total of 413 samples collected in 48 different sites. Detailed data is given in Table 1.

The sampling stations are classified in two types according with the directive 1999/30/CE (Council Directive, 1999), (i) emission sources: background (F), traffic (T) and industrial (I); (ii) sampling site location: urban (U), suburban (S), rural (R). A binomial code was used to represent both sources, such as urban traffic (UT), suburban traffic (ST), rural traffic (ST), urban industrial (UI), suburban industrial (SI), rural industrial (RI), urban background (UF), suburban background (SF) and rural background (RF), see Table 1. In the majority of cases, sampling points corresponding to urban or suburban sites affected by industrial sources or traffic (Air quality infromtion databank, 2017). In this work, a complete map including previous sites reported in 1994 and 2004 (Abad et al., 2004, 2007) and the new data from 2005 to 2015 is presented (Fig. 1), considering the mean values of fg I-TEQ/m$^3$ by location (1994 to 2015). The Fig. 1A and B, present the results for the provinces of Barcelona and Tarragona since many of the sites are in these two provinces.

The sampling device consisted of a high-volume sampler (HVS) purchased from MCV (Barcelona, Spain). A glass fiber filter was placed on the HVS head followed by polyurethane foam (PUF), previously cleaned with acetone and toluene, as an adsorbent. The process was controlled by spiking the PUF with known amounts of 2,3,7,8-$^{37}$Cl$_4$-tetrachlorodibenzo-*p*-dioxin (CSS standard solution, Wellington Laboratories Inc., Guelph, Canada). The HVS was connected to a vacuum pump to collect a volume of air between 1000 and 1600 m$^3$ in 24 h at a sampling flow rate of 45–68 m$^3$/h (Bolt and de Jong, 1993; Abad et al., 1997a, 1997b).

### 2.2. Extraction and cleanup

Prior to the extraction process, the PUF and the filter were spiked with known amounts of mixtures of $^{13}$C$_{12}$-PCDD/Fs (EPA-1613LCS, Wellington Laboratories Inc., Guelph, Canada) and then extracted using Soxhlet with 400 mL of toluene (Sigma-Aldrich, Germany) during 24 h. The extract was concentrated in a rotatory evaporator (Büchi, Switzerland) until 1–2 mL approximately. Extracts were further cleaned with a manual clean-up based on the use of multilayer silica, basic alumina and carbon adsorbents. Initially extracts were transferred to a multilayer silica (Sigma-Aldrich, Germany) column (composed by silica gel modified with sulphuric acid (44%, w/w), neutral silica gel and silica gel modified with sodium hydroxide (33%, w/w)) coupled to a basic alumina (MP Biochemicals Germany GmbH, Eschwege, Germany) column (Abad et al., 2007). A first fraction of 90 mL of hexane (Sigma-Aldrich, Germany) and a second fraction of 75 mL of a mixture of hexane:dichloromethane (9:1) were discarded. After that, PCDD/Fs were eluted from the basic alumina column with 120 mL of hexane:dichloromethane (1:1). The PCDD/F fraction was purified using a carbon column (Carbopack C 80/100 mesh, Supelco, Bellefonte, PA, USA), PCDD/Fs were eluted using 75 mL of toluene. Finally, the extracts were rotary concentrated and transferred into vials using hexane. Then, the remaining solvent was reduced to dryness by a gentle stream of nitrogen. To evaluate the recovery rates, final extracts were reconstructed in a known amount of internal standard, formed by the mixture of labeled $^{13}$C$_{12}$-PCDD/Fs (EPA-1613ISS, Wellington Laboratories Inc., Guelph, Canada).

### 2.3. Instrumental determination

Instrumental analysis was based on the use of high resolution gas chromatography coupled to high resolution mass spectrometry (HRGC–HRMS). Analyses were performed on an Agilent 6890NT gas chromatograph (Agilent, Palo Alto, CA, USA) coupled to an Micromass Ultima NT (Waters, Manchester, UK) high resolution mass spectrometer (EBE geometry) controlled by a Masslynx data system and on a Trace GC Ultra gas chromatograph coupled to a DFS high resolution mass spectrometer (BE geometry) controlled by a Xcalibur data system (Thermo Fisher Scientific, Bremen, Germany), both at 10,000 resolving power (10% valley definition). Chromatographic separation was achieved with a DB5-MS (J&W Scientific, CA, USA) fused-silica capillary column