

DIOXINS, FURANS AND DIOXIN-LIKE PCBs IN AMBIENT AIR FROM CAMP DE TARRAGONA (CATALONIA, SPAIN). SEASONAL VARIATION.

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Introduction

Quality of ambient air and levels of pollutants in Catalonia is controlled by Environment Department (Departament de Medi Ambient i Habitatge, Generalitat de Catalunya) through the Air Pollution Monitoring and Forecasting Network. In this framework, our study was focused on the characterization of PCDD/F and dioxin-like PCB levels in Camp de Tarragona, a high industrialized area in the South of Catalonia (Spain). Since some authors have detected seasonal influence on the levels of these compounds in air^{1,2}, the study considered this factor.

Materials and Methods

Sampling

Ambient air was sampled in five locations in Camp de Tarragona (Catalonia, Spain). This is a high industrialized area (petrochemical industries, incineration plants, etc.), with additional impact of traffic (highway and road network). Sampling stations were catalogued following two criteria: emission sources (background, traffic and industrial sources) and sampling site location (urban, suburban and rural). The classification of the sampling points studied is shown in Table 1. Sampling were carried out in two successive years (2005 and 2006) and in two seasons each year (autumn-winter and summer) in order to study possible seasonal variation.

Table 1. Sampling points

Location	Classification	Autumn/Winter samples	Summer samples
A	Background/Urban	3	3
B	Traffic/Suburban	3	3
C	Industrial/Suburban	4	4
D	Industrial/Suburban	2	2
E	Industrial/Suburban	2	2

Sampling was performed through the control services of Environment Department of Catalan Government (Departament de Medi Ambient i Habitatge, Generalitat de Catalunya). Sampling devices consisted of a high volume sampler (MCV, Barcelona, Spain). Particle phase was retained by a quartz-fibre filter, followed by a polyurethane foam (PUF) block for vapour phase absorption. Previous to the sampling, adsorbent was cleaned and spiked with a labelled ¹³C₁₂-PCDF standard (¹³C₁₂-1,2,3,7,8-PeCDF, ¹³C₁₂-1,2,3,7,8,9-HxCDF and ¹³C₁₂-1,2,3,4,7,8,9-HpCDF) (Wellington Laboratories, Canada) to control the sampling process.

Analysis

Analytical procedure was based on international methods (US EPA 1613, UNE-EN 1948) and consisted of following steps; (1) pre-treatment of different parts of the sample, (2) spiking with ¹³C₁₂-labelled extraction standards (Wellington Laboratories, Canada), (3) Soxhlet extraction with toluene for 48 h, (4) extract clean-up in multilayer silica column and pre-packed graphitized carbon tubes (SPE-ENVICarb, Supelco, USA), (5) final concentration and ¹³C₁₂-labelled recovery standard addition, (6) instrumental analysis by HRGC-HRMS in a RTX-5 capillary column (60 m, 0.25 mm, 0.25 µm, Restek, USA) and DB-Dioxin (60 m, 0.25 mm, 0.25 µm,

J&W Scientific, USA), (7) quantification by isotopic dilution method. PCDD/F analysis was carried out for all the samples, while dioxin-like PCB analysis was performed only in some of them. In this case, an additional fractionation to separate DL-PCB was carried out by HPLC equipped with a pyrenyl-silica column³.

Results and Discussion

PCDD/F concentration

PCDD/F concentrations obtained in the samples, organized by location and date, are shown in Figure 1.

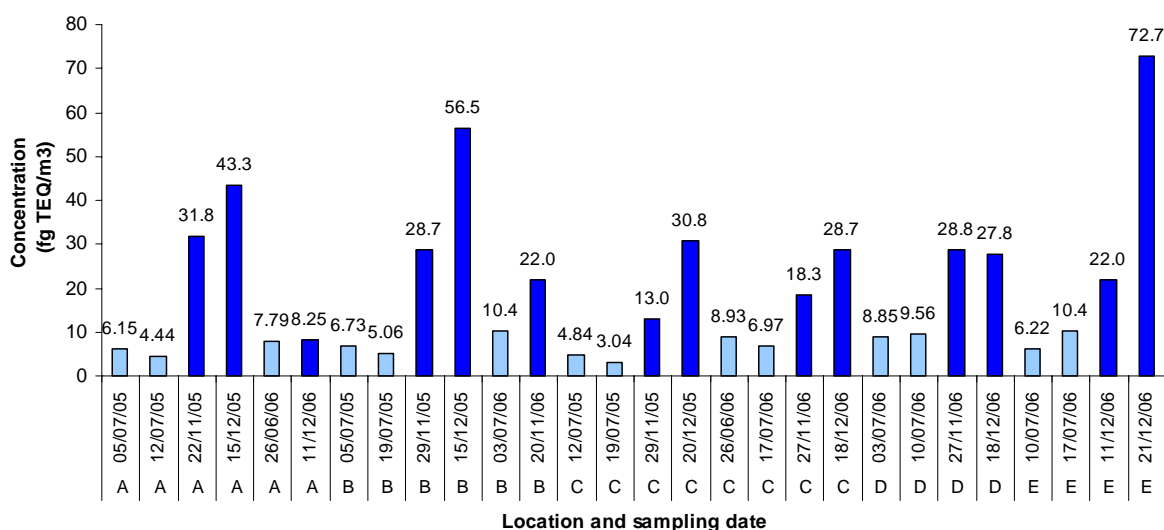


Figure 1. PCDD/F concentration (fg TEQ/m³), organized by location and sampling date (light blue: summer samples, dark blue: autumn/winter samples)

Levels of PCDD/Fs were medium-low compared to those published in literature^{1-2,4-9}. No main difference was observed between locations. Concentrations detected in summer samples (range: 3.04-10.4 fg TEQ/m³; average: 7.10 fg TEQ/m³; mean: 6.85 fg TEQ/m³) were lower than those detected in autumn-winter (range: 8.25-72.7 fg TEQ/m³; average: 31.6 fg TEQ/m³; mean: 28.7 fg TEQ/m³), which also showed higher dispersion in the values. These differences can be attributed to an increase of the PCDD/F sources in winter, lower dispersion of the pollutants in winter and higher degradation in summer.

PCDD/F partitioning between particle and vapour phase was studied in location B. Figure 2 shows seasonal differences in the homologue distribution in each phase. In summer sample, lower chlorination PCDD/Fs (tetra- and penta-) were mainly in vapour phase while PCDD/F of higher chlorination degree were mainly detected in particle phase. In winter sample, only significant amounts of TCDD/F were detected in vapour phase (20-30%). Considering TEQ values, 61% of TEQ were in particulate phase in summer, while in winter this value increased to 97%.

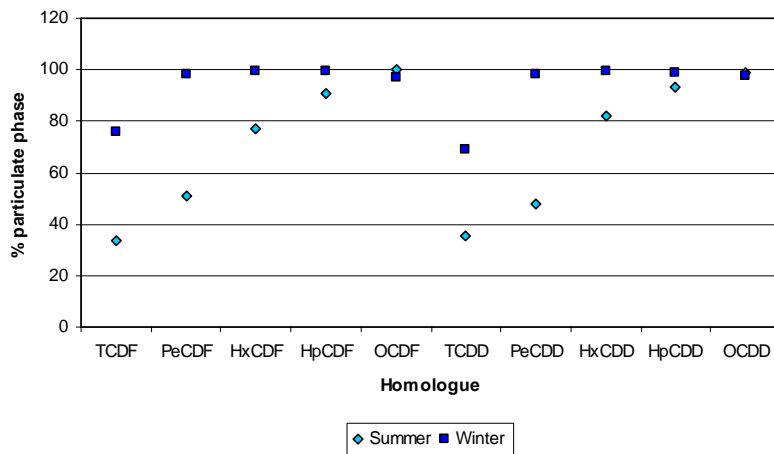


Figure 2. PCDD/F partitioning between particle and vapour phase in summer and winter samples.

Dioxin-like PCB concentration

PCDD/F concentrations obtained in the samples analysed, organized by location and date, are shown in Figure 3.

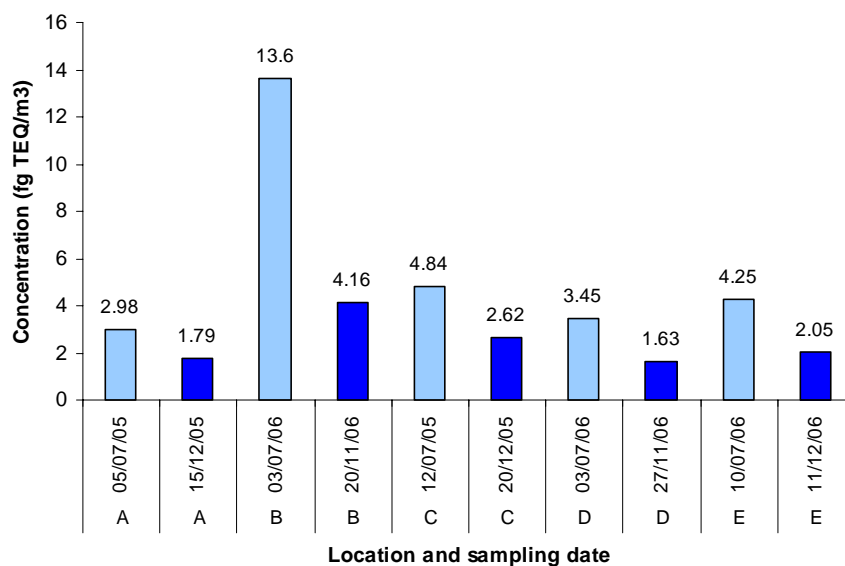


Figure 3. PCDD/F concentration (fg TEQ/m³), organized by location and sampling date (light blue: summer samples, dark blue: autumn/winter samples)

Dioxin-like PCB concentrations, expressed in fg TEQ/m³, were low. However, in some samples, they contributed more than 50% to total concentration of TEQ (Figure 4), especially in summer samples.

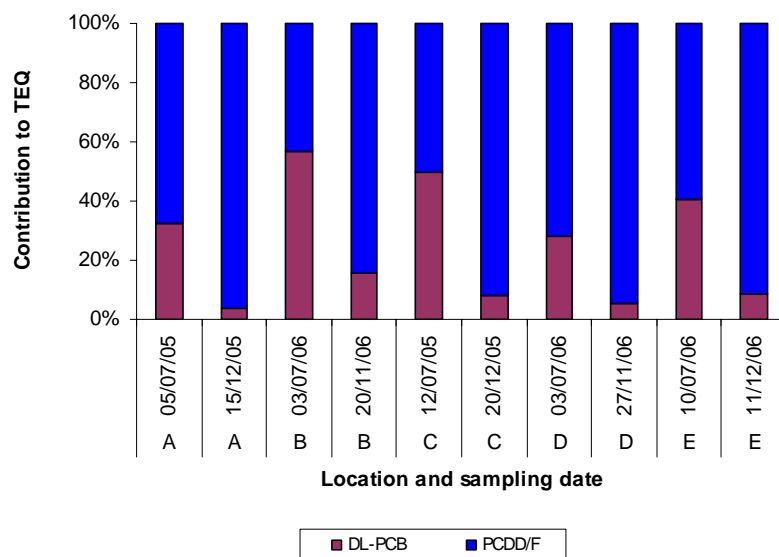


Figure 4. PCDD/F and dioxin-like PCB contribution (%) to total TEQ concentration in air samples

Concentration detected in summer samples were higher (range: 2.98-13.6 fg TEQ/m³; average: 5.82 fg TEQ/m³; mean: 4.25 fg TEQ/m³) than those detected in winter (range: 1.63-4.16 fg TEQ/m³; average: 2.45 fg TEQ/m³; mean: 2.05 fg TEQ/m³). These differences could indicate that main source of PCB to air was evaporation from soils, increased in summer due to higher temperatures.

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