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Dioxins and furans in the atmosphere of São Paulo City, Brazil

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Abstract

Air samples were collected simultaneously at three urban sites in São Paulo City, Brazil, in winter, spring, summer and fall (in 2000 and 2001). Andersen PUF samplers were used for gas and particles sequential sampling. Samples were analyzed using HRGC/HRMS according to US EPA Method 8290. The greater metropolitan area of São Paulo is the largest industrialized region of Latin America and has a highly polluted atmosphere. Concentrations of dioxins and furans, which are well-known toxic chemicals, ranged from 1.14 pg m^{-3} to 13.8 pg m^{-3} (0.047 pg I-TEQ m^{-3} to 0.751 pg I-TEQ m^{-3}). Principal component analysis showed that all the variables are highly correlated with one another except the 2,3,7,8-TCDD one. This is consistent with the similar concentration profiles observed for the tetra, penta, hexa, hepta and octa-homologous groups of the three sampling sites studied. At all sites, the most abundant compounds were the hepta and octa congeners. The 2,3,4,7,8-PeCDF accounted for 37–46% of the total toxicity and the 2,3,7,8-TCDD accounted for 7–16%. Highest mass concentrations of PCDD/Fs were found in the site where there is influence of industrial activities and heavy vehicular traffic fueled by gasohol, diesel, and ethanol.

Keywords: Urban air pollution; PCDD; PCDF; São Paulo City; Principal component analysis

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), commonly known as dioxins and furans are of non-natural origin and extremely persistent in the environment. Among 2,3,7,8 substituted toxic congeners, the 2,3,7,8-TCDD is the congener of highest toxicological significance. They have been detected in sediment, air, water, animals and plants. These pollutants are primarily emitted to the atmosphere from combustion processes. The presence of a chlorine donor in combustion seems to be the major source of their release. High levels are emitted from incineration of municipal, clinical and industrial wastes as well as in chlorine production, metal smelters, paper and pulp industries, petroleum refining processes, vehicle emissions, accidental fires, and combustion of

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biomass and biogenic fuels (De Assunção and Pesquero, 1999; Kouimtzis et al., 2002).

Urban measurements of the atmospheric PCDD/Fs in several cities have been reported recently (Mandalakis et al., 2001; Sin et al., 2002; Chang et al., 2003), but only few measurements have been carried out in São Paulo, Brazil (CETESB, 1996). To evaluate the chemical profile from a megacity with serious air pollution problems, dioxins and furans were analyzed on atmospheric particulate matter and gaseous air collected from a major South American city São Paulo, Brazil, whose population of ~16.3 million is exposed primarily to industrial and motor vehicle emissions. The urban area of São Paulo City has an unconventional mixture of vehicle types, in which a variety of fuel blends, including oxygenated ones, are used (Montero et al., 2001). For example, approximately 62% of the motor vehicles are fueled with gasohol (gasoline + 20–22% anhydrous ethanol), 8% with diesel and 30% with ethanol.

The goal of this article is to report the atmospheric PCDD/Fs pattern in highly polluted urban areas of São Paulo City. Measurements of these toxic pollutants were carried out in winter, fall, spring and summer. Occurrence of PCDD/Fs levels at a residential site located near a municipal incinerator, in downtown and in an area with mixed commercial and industrial activities is presented. PCDD/Fs levels and meteorological conditions, as well as their possible emission sources are discussed.

2. Experimental section

2.1. Sampling

In this work, three urban sites in São Paulo City were chosen on the basis of local differences in the type, distribution, and proximity of emission sources, as well as differences in wind direction frequencies.

The sampling site 1, very close to downtown, located in the park of the School of Public Health of the University of São Paulo, is near the confluence of two main streets with intense vehicular traffic where circulate many buses fueled with diesel and cars fueled with gasohol or ethanol. The area receives a significant contribution of vehicular emissions and there is no industrial activity in its immediate vicinity. Air quality data provided by monitoring station of the State Environmental Protection Agency (CETESB) located in the central area of the city (downtown) are very similar to those of site 1 and, for this reason, site 1 was assumed in this study as a downtown area (CETESB, 2002).

The sampling site 2 is a residential area, which can be considered potentially impacted by many different types of sources. The site is ~1 km NW of a health service waste incinerator used to process approximately 90 metric tons of waste per day without air pollution control system. During this study, unexpectedly, real work capacity of this incinerator was gradually diminished.

The sampling site 3, located in an area with industrial and commercial activities, receives impact from local emissions from a glass industry, non-ferrous foundry and rubber products plant as well as motor vehicular exhaust emissions from diesel heavy-duty vehicles and ethanol- and gasohol-light-duty vehicles. The sampling local is ~50 m from a major highway that has a constant dense vehicular traffic. Site 3 is distant 6.1 km NNW from site 1.

Sampling of dioxins and furans was performed according to US EPA Method TO-9A (US EPA, 1999) using Andersen GPS1 Samplers equipped with quartz micro fiber filters for particle collection and a polyurethane foam plug for gas retention. Simultaneous 24 h-samples were collected at three sampling sites in November 29, 2000, February 21, May 30 and August 28, 2001 (total number of samples taken = 12). Samplers were calibrated before and after sampling.

At site 2, inhalable particulate matter was collected using a wedding PM_{10} critical flow high volume sampler with glass–fiber filter. PM_{10} 24 h-samples were collected at a flow rate from 1.17 to 1.19 $m^3 min^{-1}$ in parallel with dioxins and furans sampling. The sampler was calibrated using an U-tube water manometer before and after sampling. The filters were weighed before and after sampling in a Mettler Toledo AG-204 analytical balance with a precision of 0.1 mg. Before weighting, filters were placed in a desiccator for 24 h for moisture removal. For the correlation study, PM_{10} data used for sites 1 and 3 were provided by CETESB monitoring stations located near sites 1 and 3.

2.2. Extraction and gas chromatography/mass spectrometry analysis

Prior sampling, filters and PUF cartridges were cleaned and spiked with 4 ng of $^{13}C_6$ 1,2,3,7,8,9-HxCDD (field surrogate). After sampling, samples and blanks were placed in an original glass container and wrapped with aluminum foil. The PCDD/Fs analyses were carried out in a laboratory (Analytical Solutions Laboratory) in Rio de Janeiro City, Brazil, according to the US EPA Method 8290 (US EPA, 1994). Samples were transported in a refrigerator with dry ice. Each filter and the corresponding PUF were combined and spiked with twelve $^{13}C_6$PCDD/F internal standards, and then Soxhlet extracted with dichloromethane for 16 h. Each extract was then cleaned-up in a sulfuric acid–silica gel column using hexane as eluent and a Florisil column using dichloromethane as eluent. The extracts were concentrated to almost dryness and $^{13}C_6$-1,2,3,4-TCDD was added in 15 μl of nonane immediately before analysis.