PCDD/F AND WHO-PCB CONTAMINATION IN AN INDUSTRIALIZED AREA IN BRAZIL FIRST RESULTS OF ATMOSPHERIC MONITORING AND THE USE OF TILLANDSIA USNEOIDES (L) AS BIOMONITOR

Márcia de Souza Pereira[1], Ulrich Waller[2], Werner Reifenhäuser[2], João Paulo Torres[3], Olaf Malm[3], Wolfgang Körner[2]

[1]Departamento de Geoquímica – Instituto de Química, 5º andar, Universidade Federal Fluminense. Outeiro de S.J. Baptista S/N, Centro, cep:24020-007, Niterói, RJ, Brazil
[2]Bavarian Environmental Protection Agency, Bürgermeister-Ulrich-Str. 160, D-86179 Augsburg, Germany
[3]Instituto de Biofísica Carlos Chagas Filho, CCS-UFRJ. Ilha do Fundão, Rio de Janeiro, CEP: 21941-900, Brazil

Introduction

A major issue of concern in developing countries like Brazil is to conciliate increasing industrialization rates to secure health and environmental standards already required to promote the free market among countries. This was pointed out during the United Nations Conference on Environment and Development in Rio de Janeiro in 1992 (Agenda 21). There it became clear that Brazil needs to develop better methods and techniques for environmental monitoring in order to control pollution sources and promote sustainable development. Among dozens of different kinds of persistent organic pollutants, polychlorinated dibenzodioxins and dibenzofurans (PCDD/PCDF) and polychlorinated biphenyls (PCB) are a matter of great concern due to their persistence, bioaccumulation and toxicological properties. PCDD and PCDF are unwanted by-products from the combustion of organic material containing trace amounts of chlorine set free in both stationary thermal sources and diffuse fuel burning. They can also be present as unwanted by-products of various industrial and metallurgical processes and metal recycling and smelters. PCB are ubiquitous

contaminants of the environment and can be produced during thermal processes. In spite of their high environmental persistence and relevance in human health concerns, legal aspects regarding maximum emission limits and control of these contaminants are absent in Brazil at present. Moreover, the absence of adequately equipped laboratories and human resources together with the high costs associated hampers the research and monitoring of these contaminants in Brazil.

The present work is a first report of the monitoring of total deposition rates of PCDD/PCDF and PCB in Volta Redonda City, a highly industrialized area in Rio de Janeiro State. Simultaneously, the use of an endemic Bromeliad species, *Tillandsia usneoides* (L), an epiphytic bromeliad, as a possible bio-monitor for persistent organochlorine compounds was investigated.

Materials and Methods

PCDD/PCDF, dioxin-like PCB and 6 indicator PCB were analysed in deposition samples. Due the high precipitation indexes commonly found in Brazil and the absence of suitable sophisticated sampling equipment, the collection method described by Mahnke[1] was adapted for monitoring PCDD/PCDF, PCB and PAH in total deposition in Brazil. Polyethylene funnels covered with polyurethane foams (effective area = 0.36 m^2) were set up. The collectors were placed 1.5 – 2.0 m above ground in order to avoid possible losses due to flooding. At the same time, a covered five-trap system containing 250 g (wet mass) *Tillandsia Usneoides* (L) was hung up besides the deposition collector system. The trap system was covered with an aluminum shed in order to prevent vertical exposure and runoff and to guarantee that only contaminants coming from ambient air were collected. The *Tillandsia usneoides* samples were obtained from the Botanic Garden of Rio de Janeiro. Four deposition and biomonitoring systems were installed in Volta Redonda, a highly industrialized city covering 0.4% of the area of the Rio the Janeiro State. The city has its economy based mainly in the metallurgical industry, steelworks and cement production. Additionally, two sampling systems were set up in the Itatiaia National Park, a nature reserve at a distance of about 65 km from Volta Redonda, used as a baseline site for the region. Samples were collected during 78 days in winter (June - August 2003) and 114 days in summer (December 2003 – February 2004).

After exposure, plant samples were freeze-dried. When necessary, PU foams were placed in a high ventilated oven at 50° C for 24 hr. Samples were spiked with all 17 2,3,7,8-substituted PCDD/PCDF $^{13}C_{12}$-labelled standards as well as 12 WHO-PCB and 6 indicator PCB congeners. Samples were then extracted with toluene in a Soxhlet apparatus for 24 hr. Purification and fractionation methods for PCB and PCDD/PCDF are described in Kerst et al.[2]. PCDD/PCDF were

analyzed by high-resolution capillary gas chromatography coupled with high-resolution mass spectrometry (HRGC/HRMS). Gas chromatographic separation was performed on a 60 m SP-2331 and a 60 m DB-XLB capillary column (PCDD/F) and on a 60 m DB-XLB column (PCB).

Results and Discussion

Table 1 shows the toxicity equivalent concentrations (TEQ) of PCDD/PCDF of both deposition and biomonitor samples measured at four different points, three in Volta Redonda city (V.R.) and one in the Nature Reserve of Itatiaia, taken during the dry season (winter). WHO-PCB TEQ concentrations are shown for winter and summer. The TEQ levels of PCDD/PCDF in the deposition samples in winter range from 0.10 to 1.9 pg WHO-TEQ/(m^2 day). These deposition rates are similar to those currently found in southern Germany[3]. However, this comparison must be considered with caution due to the different sampling methods and exposure time used in Brazil and Germany and possible losses during the long exposure time of the Brazilian deposition collectors. The WHO-PCB deposition rates in winter and summer range from 0.14 to 2.8 pg WHO-TEQ/(m^2 day) and 0.74 to 15.1 pg WHO-TEQ/(m^2 day), respectively.

Biomonitor samples show PCDD/PCDF levels ranging from 1.8 to 14.6 ng WHO-TEQ/kg dry matter (d.m.). For WHO-PCB, TEQ levels of 1.8 to 11.4 ng WHO-TEQ/kg d.m. in winter and 2.9 to 17.4 ng WHO-TEQ/kg d.m. in summer were observed. The WHO-PCB account for 25 to 85% of the total TEQ found at each site. The high concentrations of WHO-PCB found in Volta Redonda, (sites 1 and 2) may indicate that a specific contamination source exists, but more studies are needed to clarify that. A comparison between both places shows that TEQ concentrations of PCDD/F found in biomonitor samples in Volta Redonda in winter are up to 8 times higher than those found in the Itatiaia Nature Reserve. In the case of WHO-PCB, a factor of 1.5 to 6 was observed in winter. In summer, PCB levels in the Itatiaia Nature Reserve were about 6-fold higher than in winter and in the same range as in Volta Redonda.

Differences in the concentrations between the sampling stations in Volta Redonda were noted and are likely related to the distance from the main metallurgical industry in the region and the predominating wind

direction there. The low PCDD/F deposition rates found at site 1 in Volta Redonda in winter, in contrast to high levels in the corresponding biomonitor sample, may be due to losses during the sampling period. This site is one of the most polluted places in Volta Redonda due to the nearby location of metallurgical industry and the predominant wind currents. At a first look, it may be concluded that the advantageous location of site 2 (located lee to the same industry) would be responsible for the low PCDD/F deposition rates in winter found there. However, when the PCB deposition rates in winter and summer are taken into account, it became obvious that problems during the sampling period must have taken place. This is supported by the minimal variation observed in the WHO-PCB concentrations found in the biomonitor samples at all sites in Volta Redonda in winter and summer. The WHO-PCB deposition rate at site 2 in summer is 44 times greater than in winter, whereas no significant difference was observed between the concentrations found in the corresponding biomonitor samples.

Although a comparison of POP levels in different plant species must be performed with some caution, the results indicate that PCDD/PCDF concentrations in *Tillandsia usneoides* in the region of Volta Redonda are about 10 - 40 times higher than those currently found in standardized cultures of grass and green cabbage at urban stations in Bavaria, southern Germany[2]. In the Itatiaia Nature reserve the levels are about 5 – 10 times higher.

Table 1: TEQ concentrations of PCDD/PCDF and dioxin-like PCB in total deposition and *Tillandsia usneoides* samples.

	Site 1 (V.R.)		Site 2 (V.R.)		Site 3 (V.R.)		Site 4 (Itatiaia)	
	Deposition pg/m^2 day	Biomonitor ng kg^{-1}	Deposition pg/m^2 day	Biomonitor ng kg^{-1}	Deposition pg/m^2 day	Biomonitor ng kg^{-1}	Deposition pg/m^2 day	Biomonitor ng kg^{-1}
WHO-TEQ PCDD/F (winter)	0.33	14.6	0.10	2.15	1.90	6.22	0.10	1.75
WHO-TEQ PCB (winter)	2.11	7.51	0.14	11.4	2.76	2.70	0.28	1.82
WHO-TEQ PCB (summer)	15.1	17.4	6.18	12.9	4.34	2.92	0.74	11.5

Figure 1 shows the mass fragmentograms of the TCDD/TCDF, PeCDD/PeCDF and HxCDD/HxCDF from both a deposition and a biomonitor sample from one site in Volta Redonda. All samples show a thermal isomer profile with the predominance of PCDF over PCDD. Moreover, the characteristic 2,6-isomer profile in the TCDD group in all samples including those from Itatiaia exclude diffuse sources such as fossil fuel burning. Such a profile indicates stationary sources with thermal processes occurring above 700 °C as main sources[4] of PCDD/F in the region.

Regarding the concentrations of PCDD/PCDF and PCB as well as the ability to preserve the isomer and homologue pattern, *Tillandsia usneoides* reveals to be excellently suited as a sensitive, reliable and low-cost biomonitor for airborne persistent organochlorine compounds in tropical climates.

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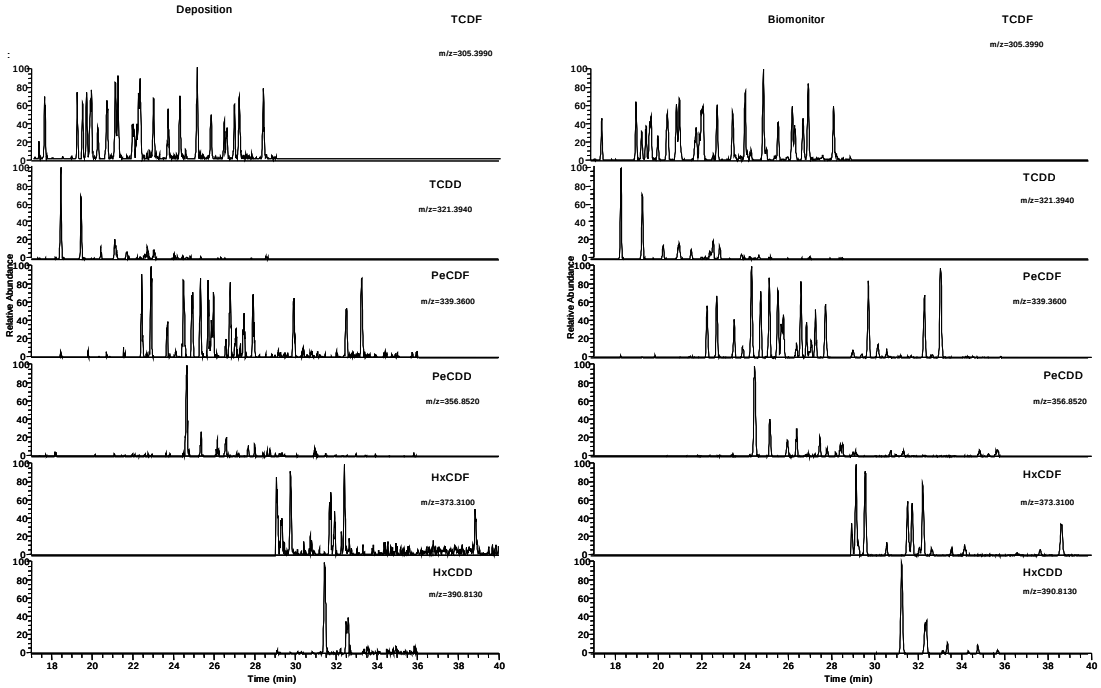

Figure 1: Mass fragmentograms of the TCDD/TCDF, PeCDD/PeCDF and HxCDD/HxCDF from a deposition and the corresponding biomonitor sample from one site in Volta Redonda.