ANALYSIS OF PBDEs IN PASSIVE AIR SAMPLES TO SUPPORT THE GLOBAL MONITORING PLAN UNDER THE STOCKHOLM CONVENTION ON PERSISTENT ORGANIC POLLUTANTS

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Introduction

The Stockholm Convention on Persistent Organic Pollutants (POPs) entered into force on 17 May 2004. The Convention aims to protect human health and the environment from negative effects of POPs by reducing or eliminating their production, use and releases to the environment[1]. Today, in May 2012, 177 countries are party to the Convention. Parties of the Convention have agreed that they need a mechanism to measure whether the objective of POPs elimination is reached Article 16 of the Stockholm Convention establishes the Global Monitoring Plan (GMP) for POPs to evaluate the effectiveness of the Convention by monitoring POPs in humans and the environment. In the guidance document for the Global Monitoring Plan of POPs[2] the objective of the GMP is described as "Provide a harmonized organizational framework for the collection of comparable monitoring data on the presence of the POPs listed in Annexes A, B and C of the Convention in order to identify trends in concentrations over time as well as to provide information on their regional and global environmental transport."

The Conference of the Parties (COP) has decided to choose ambient air and human milk and/or maternal blood as the core matrices to assess temporal and spatial trends for the initial twelve POPs. Through decisions at the fourth and fifth Conference of the Parties (COP), the number of POPs listed in annexes to the Convention has increased to 22 chemicals. Subsequently, monitoring data in humans and the environment has to be generated for the newly listed POPs.

From 2009 until 2012, Chemicals Branch of the United Nations Environment Programme's (UNEP) Division of Technology, Industry and Economics has implemented projects to support developing countries in POPs analysis and monitoring. The projects were funded by the Global Environment Facility, (GEF), the principal financial mechanism to the Stockholm Convention, and the Quick Start Programme (QSP) of the Strategic Approach to International Chemicals Management (SAICM). The projects have generated data for the initial twelve POPs in human milk[3] and in ambient air, using passive air samplers (PAS) [4].

Within the capacity building and monitoring project of UNEP in the Latin American and Caribbean (GURLAC) region, the Dioxin Laboratory of Environmental Chemistry Department of the Institute of Environmental Assessment and Water Research (IDÆA) of the Consejo Superior de Investigaciones Científicas (CSIC) in Barcelona, Spain, had supported developing countries with passive air samplers and polyurethane foam (PUF) disks to capture gas-phase POPs from air. Preliminary results the have been presented at Dioxin2011 by Martrat *et al.* [5]. Certain polybrominated diphenyl ethers (PBDEs) have been listed into annex A of the Stockholm Convention by the fourth Conference of the Parties (COP4) to the Stockholm Convention on Persistent Organic Pollutants (POPs) [6]. So far, only very limited information is available on the presence of PBDEs in atmospheric samples. Here we report the results for the eight indicator PBDEs (polybrominated diphenyl ethers) and in addition for PBDE-66 and PBDE-85 that have been captured with PUFs in eleven countries in the GRULAC region.

Materials and Methods

Passive Air Samplers

Samples have been taken from a network of 14 passive air sampling stations, which were established under the UNEP/GEF and UNEP/SAICM projects. Briefly, the passive air samplers (PAS) consisted of polyurethane foam disks housed in a protective stainless steel chamber. Sampling chambers were pre-washed and solvent-rinsed with acetone by CSIC prior to shipment and installation in the developing countries. All foams were pre-

washed, cleaned (24 h extraction in acetone), wrapped in two layers of aluminium foil, placed into zip-lock polyethylene bags and kept in the freezer prior to shipment and deployment. PUF disks were deployed for four periods of three months each, starting on 1 July 2010 and ending on 30 June 2011. After three months exposure, PUFs were removed from the PAS, wrapped in two layers of aluminium foil, labelled, placed into zip-lock polyethylene bags and transported to the laboratory where they were kept in the freezer at -18 ºC until shipment and analysis.

Sample analysis

For PBDE analysis, four PUFs per site covering one year of exposure were combined in order to obtain a composite sample and analyzed in the laboratories of IDÆA-CSIC, Barcelona. PUF disks were cut into small pieces and extracted in a Soxhlet for ~24 h with toluene after being spiked with known amounts of mixtures of $^{13}C_{12}$-PBDEs (MBDE-MXFS, Wellington Lab., Guelph, Canada). The extracts were concentrated in a rotary evaporator and transferred to *n*-hexane. Next, purification and fractionation of these extracts were carried out using a silica gel column modified with sulphuric acid (44%) and a Florisil column. Instrumental conditions for PBDEs analysis by HRGC-HRMS were similar to those for dioxin like PCB and are described elsewhere[7].

Results and discussion

PAS have been used as part of the air monitoring program in Latin America and Caribbean countries from July 2010 until June 2011. The eleven participating countries in Latin America and the Caribbean included Antigua and Barbuda; Bahamas; Brazil; Chile; Cuba; Ecuador; Jamaica; Mexico; Peru; and Uruguay. The network consisted of mainly background stations without identified POPs sources nearby. Details of the network are shown in Table 1.

Table 1: Location of PAS sites in Latin American and Caribbean region

Country (ISO code)	Site
Antigua and Barbuda (ATG)	St. Phillip's
Bahamas (BHS)	Coral Harbour
Barbados (BRB)	St. James, Christ Church
Brazil (BRA)	São Paulo
Chile (CHL)	Canal Melchor
Cuba (CUB)	Havana, Cienfuegos, Sancti Spiritus, Santiago de Cuba
Ecuador (ECU)	Quito
Jamaica (JAM)	Kingston
Mexico (MEX)	Monte Azules, Chiapas
Peru (PER)	Lima
Uruguay (URY)	Montevideo

The eight PBDE congeners that are recommended for analysis in ambient air samples according to the UNEP in the Draft Revised Guidance for the Global Monitoring Plan [2] together with two additional PBDE congeners and the respective sums of congeners are shown in Table 2. The results are presented in ng per PUF, whereby four PUFs had been combined into one data point covering one year (4-times 3-months exposures). Concentrations are shown as upper-bound, *i.e.*, for not-quantifiable congeners the full detection limit is included when calculating the sum PBDE(8) or PBDE(66+85) or sum PBDE(10); concentrations below the limit of quantification (LOQ) are shown in red color in Table 2. The eight recommended, indicator PBDE congeners could be quantified in all samples and roughly are within the same order of magnitude than other intentionally produced POPs such as hexachlorobenzene, (HCB), hexachlorocyclohexanes (HCHs) or polychlorinated biphenyls (PCB); although the latter had much wider ranges in PAS samplers. The concentrations for the sum of

PBDE(8) ranged from 1.51 ng per PUF in Cuba (station at Sancti Spiritus) to 46.7 ng per PUF in Jamaica. In four samples, PBDE 85 could not be quantified (see red numbers in Table 2).
The concentrations can be compared with recent results from the Brisbane area in Australia, were concentrations of 12.7 ± 5.2 ng PUF^{-1} were detected for the sum of five PBDE congeners (PBDE 28, 47, 99, 100, 209) [8] or from a rural/remote latitudinal transect from southern UK to northern Norway[9]. As an example, Figure 1 shows a GC-HRMS chromatogram of an air sample from Antigua and Barbuda. Among all PBDE congeners, PBDE 47 (on average 41% to $\Sigma PBDE_8$) was the predominant congener in all PUF samples, followed by PBDE 99 (on average 21% to $\Sigma PBDE_8$) and PBDE 28 or PBDE 183 (on average 9% to $\Sigma PBDE_8$ for each of them) (Table 2 and Figure 2).

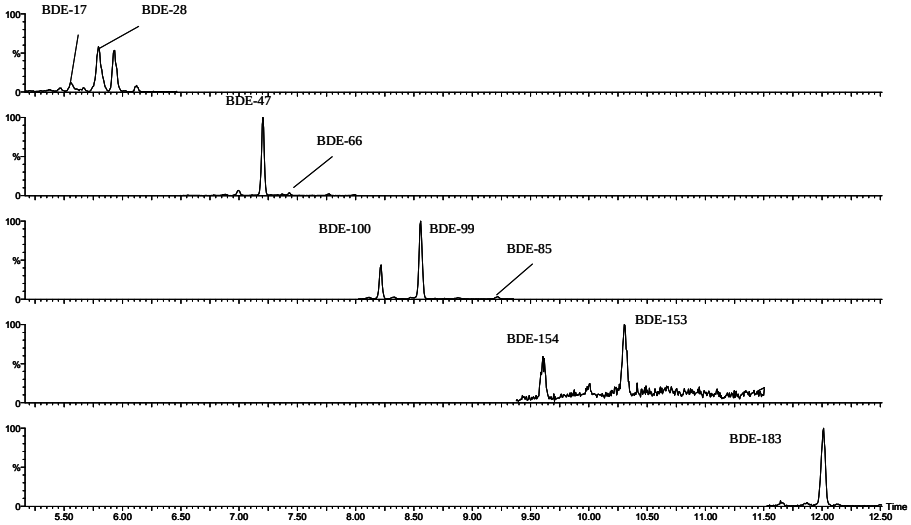

Figure 1: PBDEs HRGC-HRMS chromatogram of an extract from PUF ambient air sample

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Table 2: Concentration of PBDEs (ng/PUF) in PUFs from passive air samplers in the Latin America and Caribbean region

No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Country ISO	ATG	BHS	BRB	BRA	CHL	CUB-CF	CUB-SS	CUB-CH	CUB-SC	ECU	JAM	MEX	PER	URY
PBDE congeners recommended by UNEP														
BDE-17	0.10	0.78	0.47	0.84	0.004	0.15	0.10	0.30	0.06	0.65	2.23	0.03	3.28	1.52
BDE-28	0.21	1.43	1.91	0.91	0.05	0.24	0.14	0.44	0.11	0.73	4.20	0.08	2.31	1.52
BDE-47	1.29	9.13	7.04	6.45	0.62	0.65	0.61	2.17	1.49	2.49	22.2	2.05	9.01	3.98
BDE-99	0.75	4.39	2.60	2.94	0.46	0.27	0.19	1.10	1.28	1.10	11.5	1.77	5.11	1.89
BDE-100	0.21	1.20	1.11	0.67	0.09	0.12	0.06	0.29	0.27	0.27	2.72	0.47	1.27	0.51
BDE-153	0.23	0.88	0.45	0.48	0.16	0.30	0.09	0.13	0.19	0.90	1.48	0.83	1.27	0.40
BDE-154	0.09	0.61	0.65	0.29	0.05	0.11	0.06	0.14	0.11	0.45	1.11	0.29	0.73	0.30
BDE-183	0.54	1.34	1.02	0.61	0.33	0.77	0.26	0.16	0.30	2.46	1.23	2.73	3.14	0.67
ΣPBDE(8)	3.42	19.8	15.2	13.2	1.77	2.60	1.51	4.74	3.81	9.05	46.7	8.25	26.1	10.8
Additional PBDE congeners														
BDE-66	0.09	0.39	0.35	0.44	0.04	0.11	0.02	0.21	0.02	0.13	2.14	0.07	1.43	0.07
BDE-85	0.05	0.20	0.13	0.11	0.03	0.05	0.02	0.07	0.09	0.07	0.28	0.12	0.29	0.10
PBDE 66+85	0.14	0.59	0.48	0.54	0.07	0.16	0.03	0.28	0.11	0.20	2.42	0.20	1.72	0.16
ΣPBDE(10)	3.57	20.4	15.7	13.7	1.84	2.76	1.55	5.02	3.93	9.25	49.1	8.45	27.8	11.0

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