UNEP PROGRAM CAPACITY BUILDING PROJECT FOR THE GLOBAL MONITORING PLAN IMPLEMENTATION ON PERSISTENT ORGANIC POLLUTANTS UNDER THE STOCKHOLM CONVENTION IN   LATIN AMERICA AND CARIBBEAN

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Introduction

The Stockholm Convention on Persistent Organic Pollutants (POPs)[1] entered into force in May 2004. The Convention aims to protect human health and the environment from POPs and reduce or eliminate their production, use and release into the environment[2]. Article 16 of the Stockholm Convention establishes the need to implement a Global Monitoring Program (GMP)[3] for POPs. In order to create a national capacity in POPs analysis so that countries can contribute with their own data to the GMP, the United Nations Environment Programme (UNEP) is undertaking various projects for training, capacity building and scientific cooperation in developing countries. Presently, these projects cover the regions of Latin America and the Caribbean, Pacific Asia and Africa.

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, is cooperating with UNEP in the implementation of the Global Monitoring Program (GMP) of POPs listed in the Stockholm Convention.

In short, this collaboration includes four distinct lines of action:

1. Performing site inspections or sending out questionnaires in order to assess and identify strengths and weaknesses of the different laboratories in the Latin America and Caribbean region (GRULAC) involved in the POPs monitoring network of the countries participating in the project.

2. Conducting hands-on training workshops in the developing country laboratories and capacity building to complement their expertise to analyze POPs in these laboratories.

3. Faciliting the supply of materials and consumables needed to carry out the analysis of POPs in these laboratories.

4. Undertaking mirror analysis of national samples from the developing countries in CSIC's dioxin and POPs laboratories to compare the results with those from the developing country laboratories. Providing high quality data for countries that do not have own POPs laboratories. This is often the first POPs data for this country.

The project was carried out between March 2009 and September 2011 and is financed with funds from the Global Environment Facility (GEF), the SAICM Quick Start Programme, and the Secretariat of the Stockholm Convention

Materials and methods

Air sampling

Polyurethane foam based samplers were employed in this study. They consist of polyurethane foam (PUF) disks housed in a protective stainless steel chamber (see Figure 1). Sampling.shambers were prewashed and solvent-rinsed with acetone prior to installation. All foams were prewashed, cleaned (24 hours extraction in acetone), wrapped in two layers of aluminum foil, placed into zip-lock polyethylene bags and kept in the freezer prior to deployment. Exposed PUFs were wrapped in two layers of aluminum foil, labeled, placed into zip-lock polyethylene bags and transported to the laboratory where they were kept in the freezer at -18 ºC until analysis. All developing country laboratories were equipped with samplers and five PUF disks per sampler.

Sample analysis

For PCDD/PCDF and non-ortho PCB analysis, samples were extracted in a Soxhlet for ~24h with toluene after being spiked with known amounts of mixtures of $^{13}C_{12}$-PCDD/PCDF (EN1948 ES, Wellington Lab., Guelph, Canada) and $^{13}C_{12}$-DL-PCB (P-48-W-ES, Wellington Lab., Guelph, Canada). Further sample purification and

instrumental analysis by high resolution gas chromatography coupled to high resolution mass spectrometry (HRGC-HRMS) are described elsewhere[4].

For marker PCB analysis, the extraction and purification methodology was similar to that previously described for PCDD/PCDF and DL-PCB. Briefly, PUFs were spiked with known amounts of $^{13}C_{12}$-PCB (MBP-MXE, Wellington Lab., Guelph, Canada) and then extracted in a Soxhlet for ~24h using n-hexane: dichloromethane (1:1). After that, the extracts were rotary concentrated 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 marker PCB analysis by HRGC-HRMS were similar to those for PCDD/PCDF and DL-PCB.

Results and discussion:

Initially, a comprehensive questionnaire was sent and completed by the laboratories prior to the training. This enabled the trainers to collect general information in advance on the type of samples analyzed in the laboratory, safety issues, type of instruments used, type of gas chromatographic (GC) columns used and dimensions, extraction and clean up methods, quality assurance/quality control (QA/QC) issues, education of staff, etc. This project also included a procurement component through which consumables and analytical standards could be sent to the laboratories. On-site training sessions were completed, which helped to prepare the laboratories for the analysis of POPs in air, fish, breast milk and sediment samples. All courses lasted for five days. The training consisted of a theoretical part (lectures and discussion) and a practical hands-on part in the laboratory.

From the information assembled through the questionnaires and then confirmed by the training sessions in the developing country laboratories, it was seen that all laboratories were equipped with instrumentation suitable for POPs analysis; *i.e.,* capillary gas chromotographs and electron capture or mass-selective detectors, respectively. According to instrumentation present, there were seven laboratories that used ECD for POPs analysis, seven laboratories with MS detection whereby one laboratory expressed its desire to analyse PCDD/PCDF and dioxin-like PCB, and one laboratory equipped with high resolution mass spectrometer. The latter one expressed interest in the training of dioxin analysis in environmental matrices, especially in ambient air samples. The training also revealed that the working conditions (laboratory space, fume hoods, safety regulations, temperature, etc.) in most of the laboratories satisfied usual requirements. However, also several deficiencies were identified. Lack of sufficient number or good quality of consumables, *e.g.,* GC columns of adequate dimensions, certified standard, laboratory reference materials, coolers, glass stoppers, water baths, septa. In addition, there was also an obvious need for training of staff such as on replacing dirty liners and septa.

In total, eight training sessions were held in eight countries. On the very positive side, it is concluded that all staff showed a very positive attitude during the training. It was observed that the knowledge within a laboratory often varied: whereas the scientists had a good understanding of the implications of each step of POP analysis, technicians sometimes were at more basic level. Often, they were trained on the job while working in the laboratory and did not receive further training. Consequently, five days of dedicated POP analysis training was too short for them to attain the desired level. Nevertheless, improvements were seen.

PAS have been used as part of the air monitoring program in Latin America and Caribbean countries from July 2010 until June 2011. A network of 12 sites covering mainly background stations - representing urban to rural sites and including mountain sites – contributes to the project (Table 1).

Preliminary results from the first sampling campaigns showed that PCB and PCDD/PCDF could be quantified in all samples and in all countries. Concentrations of the sum of the seven PCB congeners recommended for analysis under the Stockholm Convention, found in the PUF from the first 3-months exposure time are shown in Table 2. For the ΣPCB_7, the highest concentration was found at the urban station of Havana, Cuba with a mean value of 640 ng PUF^{-1}. The lowest concentration with less than 1 ng PUF^{-1} was found in Mexico.

Table 3 shows the results for the dioxin-like POP as pg WHO_{1998}-TEQ PUF^{-1}. For PCDD/PCDF, the highest concentration was found in Jamaica with a mean value of 612 pg PUF^{-1}, followed by Peru (439 pg PUF^{-1}) and Brazil (267 pg PUF^{-1}). These concentrations correspond to 36, 23, and 16 pg WHO_{1998}-TEQ PUF^{-1}, respectively. The mass concentrations of the 12 dl-PCB were higher than the mass concentrations of the 17 PCDD/PCDF congeners. However, expressed as TEQ and with the exception of Brazil, the TEQs from PCB were lower than from PCDD/PCDF. The total TEQs were in a quite narrow range from 20 pg WHO_{1998}-TEQ PUF^{-1} to 52 pg WHO_{1998}-TEQ PUF^{-1}.

References:
1. Environmental Health Series No 34 (1989): Levels of PCBs, PCDDs, and PCDFs in breast milk, WHO Regional Office for Europe, Copenhagen, Denmark
2. United Nations Environment Programme (UNEP), 2001. Stockholm Convention on persistent organic pollutants (POPs), Text and Annexes (http://chm.pops.int).
3. United Nations Environment Programme (UNEP), 2007. Guidance on the Global Monitoring Plan for Persistent Organic Pollutants. Preliminary version, February 2007.
4. Abad E, Sauló J, Caixach J and Rivera J (2000). J. Chromatogr. A 893:383-391

Figure 1. PAS Sampler.

Table 1. Sampling sites.

Country/ PAS site	Latitude	Longitude	Altitude
Antigua and Barbuda	61° 45' 27.932 W	17° 4' 44.77 N	16'5''
Brazil/ São Paulo	-23°33' 41.32"	-46° 42'7.51''	
Ecuador/ Quito	0°13'12"S	78°30'36"W	
Jamaica/ Kingston	17° 59'50''N	76°47'22''W	1.6 meter from ground level
Mexico/Lacandona Rain Forest-Montes Azules, Chiapas	16°08'38.39'' N	90°54'7.64''W	150 msnm
Peru/ Lima	11°54¨S	77°3¨W	
Barbados	13.149° N	69.624° W	
Uruguay/ Montevideo	34° 50' 13.1"	56° 13' 20.8''	
Cuba (La Palma)	220 45.985' N	0830 32.666' W	45.11 m
Cuba (Havana)	23.10 N	82.21 W	50.08 m
Cuba (Cienfuegos 1)	22° 03' 59,8''N	080° 29' 56.1'' W	34.9 m
Cuba (Cienfuegos 2)	21° 55' 15''N	080° 01' 23'' W	767.335 m
Cuba (Santiago de Cuba)	20° 00' 44.5''N	075° 38' 05,3'' W	1110 m

Table 2. Concentrations of ΣPCB_7 (ng PUF^{-1}) found in the different countries during 1st sampling period (July-September 2010)

ng PUF^{-1}	ΣPCB_7
Brazil	40.5
Ecuador	9.7
Mexico	0.63
Uruguay	41.9
Antigua and Barbuda	1.9
Barbados	4.4
Jamaica	18.6
Cuba La Palma	5.8
Cuba Havana	640
Cuba Cienfuegos1	3.0
Cuba Cienfuegos2	6.3
Cuba Santiago de Cuba	4.9
Peru	49.7

Table 3. Concentrations of $\Sigma PCDD/PCDF$ and Σdl-PCB as well as WHO$_{1998}$-TEQ (pg PUF^{-1}) found in three countries (mean of one sampling periods).

pg PUF^{-1}	Brazil	Jamaica	Peru
$\Sigma PCDD/PCDFs$ pg PUF^{-1}	267	612	439
Σnon-ortho PCBs pg PUF^{-1}	382	366	1266
Σmono-ortho PCBs pg PUF^{-1}	2523	1543	8738
$\Sigma PCDD/PCDF$ pgWHO$_{1998}$-TEQ PUF^{-1}	15	23	36
ΣDL-PCB pgWHO$_{1998}$-TEQ PUF^{-1}	37	4	16
$\Sigma PCDD/PCDF$+DL-PCB pg WHO$_{1998}$-TEQ PUF^{-1}	20	30	52