UNEP's TRAINING AND CAPACITY BUILDING ON POPS MONITORING (2009-2011)

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Introduction

The Stockholm Convention on Persistent Organic Pollutants (POPs)[1] was adopted on 22 May 2001 and entered into force on 17 May 2004. As of May 2011, the Convention had 173 Parties. In order to protect human health and the environment from POPs by reducing or eliminating releases to the environment, Parties have agreed on a mechanism to measure whether this objective is reached. According to Article 16, the effectiveness evaluation consists of three elements: *(i)* Reports and other environmental monitoring information pursuant to paragraph 2 of Article 16, *(ii)* National reports submitted pursuant to Article 15, and *(iii)* Non-compliance information submitted pursuant to Article 17. Guidance for a Global Monitoring Plan (GMP) has been developed to provide comparable monitoring information on the presence of the persistent organic pollutants listed in Annexes A, B and C of the Convention. To improve the worldwide performance of laboratories and thus improve the availability of reliable analytical data and contribute to the Global Monitoring Plan, UNEP Chemicals in cooperation with partners supports this objective through the following activities:

- Developing criteria for generating high quality POPs data to be applied at the global level: Guidelines for the sampling, extraction, clean-up, separation, identification, and quantification of the initial 12 POPs have been developed
- Establishing a databank of operational POPs laboratories worldwide: the databank presently has 232 laboratories[2];
- Undertaking training and capacity building of POPs laboratories in developing countries: Expert laboratories train developing country laboratories in their own laboratories with an emphasis on ambient air (with passive air samplers) and mothers' milk, the core matrices of the GMP;
- Undertaking a First Worldwide Intercalibration Study on POPs to assess the performance of POPs laboratories worldwide and to build trust in their data;
- Providing results of POPs data especially from developing countries for further assessments at national and international levels; and
- Building networks and cooperation between POPs laboratories around the world.

From 2009 until 2011, UNEP Chemicals Branch of the Division of Technology, Industry and Economics, is implementing capacity building projects in 32 developing countries to enable them submitting their own data to the Global Monitoring Plan of POPs under the Stockholm Convention and to compare their own performance with results from experienced expert back-up laboratories[3].

Materials and methods

Intercalibration study: The First Worldwide Intercalibration Study on POPs was coordinated by IVM, Free University Amsterdam and MTM Centre, Örebro University and was implemented in two steps, an Asian component and an African/Latin American component whereby in both parts, laboratories from developed countries participated as well as laboratories from Central and Eastern European countries. The test materials comprised the following:

- Three standard solutions: Standard 1A consisted of a mixture of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/PCDF) and dioxin-like polychlorinated biphenyls (dl-PCB) in the concentration range from 10 pg/µl to 500 pg/µl (ng/ml). Standard 1B consisted of a mixture of the indicator PCB in the concentration range from 0.1 ng/µl to 5 ng/µl (µg/ml). Standard 1C consisted of a mixture of organochlorine pesticides (OCP) in the concentration range from 10 pg/µl to 50 pg/µl (ng/ml).
- Sediment originating from Norway; air-dried at 40 °C and sieved (0.5 mm pore size);
- Fish sample from the Great Lakes; freeze-dried;
- Human milk sample from Swedish mothers; frozen and stored at -20 °C before shipment; and
- Ash sample from a municipal solid waste incinerator in Sweden; dry, as received after bag house filter and wet scrubber.

The set-up of the sampling programs for ambient air through passive air sampler (PAS) and for mothers' milk follow the recommendations laid down in the Guidance document for the GMP[4].

Passive air samplers (PAS): PAS with polyurethane foams (PUF) disks to capture POPs from ambient air have been supplied to all participating countries using harmonized procedures in all countries. Each sampler is equipped with one pre-cleaned PUFs and exposed for three months. The sampling periods consisted of four exposures to cover one year. A typical sampling site had five PAS: two for basic POPs-PUFs analyzed in the back-up expert laboratory, two PAS for basic POPs-PUFs analyzed in the developing country laboratory; one PAS for dioxin-like POPs-PUFs analyzed in back-up dioxin laboratory for annual average concentration. Where dioxin laboratories existed in the developing countries – Brazil, Egypt, Jamaica – three more PAS were exposed to mirror the annual sample for dl-POPs as well as to generate 3-months quarterly results. Wherever possible, the PUF results obtained in the developing country laboratory were compared with the results from the expert back-up laboratory.

Mothers' milk samples: Mothers' milk samples were collected and analyzed using the WHO protocol[5]. Briefly, 50 mL of human milk from mothers' have delivered their first child were collected and pooled into a national sample. All national pools were analyzed in the WHO-UNEP Reference Laboratory. National developing country laboratories analyzed either the pool or the individual samples in the pool.

Training of the laboratories: Typically, one-week training courses were held in the developing country laboratory by two staff from the expert back-up laboratory. For the African and Latin-America regions back-to-back with the final results workshops, further training was organized at IVM VU University Amsterdam and CSIC Barcelona.

Results and discussion:

The analytes investigated in these projects comprise the initial twelve POPs and their main transformation products, see Table 1.

Table 1: Analytes recommended for POPs analysis according to the GMP guide (12 initial POPs)

Sum drins: Aldrin, dieldrin, endrin
Sum chlordanes: α-chlordane, γ-chlordane, *trans*-nonachlor, *cis*-nonachlor, oxychlordane
Sum DDTs: *p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT, *o,p'*-DDE, *o,p'*-DDD
Sum heptachlors: Heptachlor, *trans*- heptachloroepoxide, *cis*- heptachloroepoxide
Hexachlorobenzene
Mirex
Sum toxaphene: Parlar 26, Parlar 50, Parlar 62
Sum of polychlorinated biphenyls (PCB_7): PCB 28, 52, 101, 118, 138, 153, and 180
dl-PCB (as TEQ_{PCB}): PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189
2,3,7,8-chlorosubstituted PCDD/PCDF (as $TEQ_{PCDD/PCDF}$): 2,3,7,8-Cl_4DD, 1,2,3,7,8-Cl_5DD, 1,2,3,4,7,8-Cl_6DD, 1,2,3,7,8,9-Cl_6DD, 1,2,3,6,7,8-Cl_6DD, 1,2,3,4,6,7,8-Cl_7DD, Cl_8DD, 2,3,7,8-Cl_4DF, 1,2,3,7,8-Cl_5DF, 2,3,4,7,8-Cl_5DF, 1,2,3,4,7,8-Cl_6DF, 1,2,3,7,8,9-Cl_6DF, 1,2,3,6,7,8-Cl_6DF, 2,3,4,6,7,8-Cl_6DF, 1,2,3,4,6,7,8-Cl_7DF, 1,2,3,4,7,8,9-Cl_7DF, Cl_8DF

Intercalibration study: The results from the Asian part – 38 Laboratories during 2009-2010 - of the First Worldwide UNEP Intercalibration Study on POPs are available. The summary of RSDs for the five test matrices and the groups of POPs are shown in Table 2. The participants were not restricted in the methodology used for the analysis of the target compounds in this first UNEP intercalibration study. The use of capillary GC was considered mandatory to achieve the separation needed for an accurate determination of the analytes. The laboratories used their own extraction and clean up protocols, spiking schemes, standards and internal QA/QC. In order to assure that the target decrease of POPs concentration in the core matrices as stated in the GMP guide, namely "to show a 50 % decline in levels of the POPs over a ten year period", a stringent criterion for RSD = 12.5% was set by UNEP. As can be seen from Table 2 from the data for the Asian region, this criterion is best met by dioxin laboratories where on average by 11 laboratories a RSD of 13% is met in mothers' milk. For the same matrix and for PCB, the performance is satisfactory. Especially for real matrices and for POPs pesticides, the RSDs are still too high to allow for trend analysis.

Table 2: First Worldwide Intercalibration Study on POPs – Asia region: RSDs and number of laboratories after removing obvious outliers (** Italic, no outliers removed)*

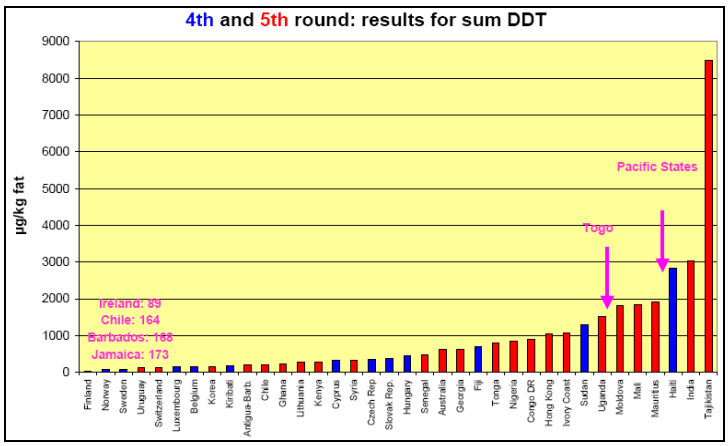
	Ash (RSD/n)		Sediment (RSD/n)		Fish (RSD/n)		Milk (RSD/n)		Standard (RSD/n)	
$TEQ_{PCDD/PCDF}$	18 %	22	19 %	19	18 %	13	16 %	11	8 %	28
TEQ_{PCB}	19 %	15	22 %	17	19 %	12	22 %	11	16 %	24
TEQ_{total}	19 %	17	17 %	16	18 %	12	13 %	11	8 %	23
PCB_7	*91 %**	9	*35 %**	16	*57 %**	12	14 %	10	12 %	22
Drins	-	-	*227 %**	4	40 %	8	29 %	10	15 %	22
Chordanes	-	-	99 %	8	26 %	8	46 %	9	17 %	19
DDTs	-	-	29 %	16	30 %	9	31 %	10	14 %	20
HCB	-	-	26 %	14	30 %	9	25 %	9	14 %	22
Mirex	-	-	22 %	5	29 %	9	29 %	9	9 %	18

The locations of the PAS in Africa and Latin America are shown in Figure 1, quarterly samples from at least one location per country are taken. Exposure periods were from 1 April or 1 July 2010, *resp.*, for one year. Eight countries in the Pacific Islands will further contribute with two sampling periods representing the dry and the wet season. PUFs were analyzed for basic POPs using capillary GC and ECD and using HRGC/HRMS for dioxin-like POPs.

Figure 1: Locations of PAS in Latin America/Caribbean and Africa (copyright map: Google maps)

The results from the first two or three exposures are available. The preliminary results show that although not all POPs were detected in all samples, PAS are a useful and cost efficient tool to characterize locations in a multitude of countries around the world. Among the OCPs, especially DDE but also DDT (in Africa), and dieldrin are frequently detected having concentrations in the ng PUF^{-1} range. PCB could be detected in all

samples[6]. From the first two exposures in Latin America, the concentrations of the sum PCB_7 were highest in the urban location of Havana, Cuba (640 ng PUF^{-1}). Dioxin-like POPs were quantifiable in all PUFs analyzed so far. The concentrations of PCDD/PCDF and dl-PCB were in the low pg TEQ range for both groups[7].



One of the striking results from this last round of WHO-UNEP study is that in recent years, higher concentrations were found than were detected in the earlier round (2003) (Figure 2). The concentrations in the pools from Tajikistan, India, and Haiti were higher than the concentrations – 2,000 µg kg^{-1} fat - found earlier in Hong Kong. However, for Hong Kong, the concentration is declining and only about half of the 2003 value.

Figure 2: Results of pooled mothers' milk samples - DDTs

The Stockholm Convention requires robust and reliable analytical data and information to monitor and evaluate progress in implementation, to enforce practical limit values, and to establish time trends. Similarly, national governments need reliable and robust analytical data as a basis for developing baselines, identifying priorities and planning appropriate actions; and to assess the effectiveness of that work. Parties to the Convention acknowledge these needs and at COP-5 endorsed the GMP and activities to support its implementation. Parties have initiated the necessary steps and are aware that trade between Parties requires mutual confidence in analytical results that confirm adherence to internationally accepted standards and permissible levels.
The experiences in these projects have been very positive, however, participating countries ask for further assistance with respect to the following:

– Monitoring and analytical capacity for persistent organic pollutants, including the new POPs;
– Regular intercalibration and QA/QC programs;
– Inclusion of more countries within regional projects.

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