

## Global Monitoring of Persistent Organic Pollutants in Air – First Observations and Future Challenges

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### Introduction

At its third session, held 30 April–4 May 2007 in Dakar, Senegal, the Conference of the Parties of the Stockholm Convention adopted decision SC-3/19 on effectiveness evaluation and a global monitoring plan on persistent organic pollutants (GMP). The GMP's objective is to collect comparable monitoring data or information on the presence of the twelve initial persistent organic pollutants (POPs) in core matrices in order to identify trends in levels over time as well as to provide information on the POPs' regional and global environmental transport. Air, human milk, and human blood were selected as the core media.

In order to establish harmonized monitoring programs, the "Guidance on the Global Monitoring Plan for Persistent Organic Pollutants"<sup>1</sup> was developed, which lays out the elements for the GMP including sampling and analytical methodology as well as statistical evaluation. The GMP guidance formulates the quantitative objective for temporal trends as follows: "To detect a 50 % decrease within a time period of 10 years with a statistical power of 80 % at a significance level of 5 %". For spatial studies "To detect differences of a factor 2 between sites with a power of 80 % at a significance level of 5 %".

Subsequently, information is gathered from ongoing monitoring programs on concentrations of POPs in these core media and new projects are initiated to generate data from regions in the world where so far no or few data exist. The first global report for the effectiveness evaluation is due in May 2009 for the fourth meeting of the conference of the parties and the data will form the baseline of POPs contamination in the core matrices.

The ambient air programs are set-up to obtain representative data for assessing time trends and regional and global transport of POPs. Ambient air also reflects the present situation in the countries since this matrix is rapidly responding to changes in source strength and does not have the "memory of accumulated past exposures" of other matrices such as mothers' milk or human blood.

### Methods

Results from different air monitoring studies using the UNEP-recommended methodology as shown below have been reviewed. There are different approaches for air monitoring with the following characteristics (Table 1):

Table 1: Types and characteristics of commonly used ambient air samplers

Type	Basic Elements	Sampling Time, Volume, Infrastructure
1. High-volume active samplers	Glass-fiber/quartz filters combined with polyurethane foam (PUF) plugs; XAD or carbon filters/disks added	Time: 1-2 days; up to one week; Volume: 600-1,500 m <sup>3</sup> /d; High demands on infrastructure
2. Passive samplers	PUF disks, XAD-based resin, LDPE with triolein; in stainless steel chambers	Time: several months to year; Volume: 0.5-4 m <sup>3</sup> /d; Low demands on infrastructure
3. Bulk deposition samplers	Frisbee-type (plastics), Bergerhoff (glass)	Time: 14-30 days Surface-based measurements; Low demands on infrastructure

The GMP guidelines<sup>1</sup> and a recent UNEP/GEF project on POPs analysis<sup>2</sup> define the instrumental needs for the analysis of POPs. Different instrumental requirements are recommended for the various POPs (Table 2).

Table 2: Recommended instrumentation (Tiers) for analysis of combinations of POPs and matrix type

POP	Matrix	Tier
POPs pesticides	Abiotic (includes air)	Labs at Tiers 1 (=HRMS), 2 (=LRMS), 3 (=ECD)
	Biota	Labs at Tiers 1, 2, 3
Toxaphene	Biota (low contamination)	Labs at Tiers 1, 2
PCB	Abiotic (includes air)	Labs at Tiers 1, 2, 3
	Biota	Labs at Tiers 1, 2, 3
	Biota (low conc., e.g., blood)	Labs at Tiers 1, 2
dl-PCB	Abiotic	Labs at Tiers 1, 2
	Biota	Labs at Tier 1, 2
PCDD/PCDF	Abiotic (except ambient air)	Labs at Tiers 1, 2
	Abiotic - ambient air	Labs at Tier 1
	Biota	Labs at Tier 1 (2)
	Stack emissions	Labs at Tier 1

Especially for POPs such a toxaphene, the analysis is complex and for PCDD/PCDF and dioxin-like PCB, the concentrations are orders of magnitude lower than for the POPs pesticides. Depending on the type of detector and the type of POP, the following limits of quantification can be achieved:

- POPs pesticides and indicator PCB: 1 pg/m<sup>3</sup> with ECD; 1 pg/m<sup>3</sup> with LRMS, and 0.01 pg/m<sup>3</sup> with HRMS
- PCDD, PCDF, dioxin-like-PCB (per congener): 100 fg/m<sup>3</sup> with LRMS, 10 fg/m<sup>3</sup> with HRMS.

## Results

Bulk deposition samplers are not designed to measure actual air concentrations of POPs but their deposition. Depending on the technology, deposition of the gas-phase POPs and POPs deposited with snow may be underestimated or lost at sampler types that do not use any storage medium like XAD to adsorb the deposited pollutants, light protection chambers for the filters, and devices to melt the snow deposited into the funnel. New technologies of deposition sampling take account of these problems<sup>3</sup>. The GMP focuses on air concentration, so bulk deposition samplers are presently not included in the UNEP GMP guidelines..

High-volume active air samplers rely on a pump to collect the particle-bound and the gaseous phase POPs from the air and concentrate them first in a fibrous or polymeric matrix and then, after extraction, in an organic solvent for subsequent chemical analysis in the laboratory. Passive air samplers (PAS) are based on the same principle, but rely on molecular diffusion rather than pumped air flow for uptake. Sampling efficiencies are different for gas and particle phase, and most PAS are inefficient collectors of particle-bound POPs. Because a PAS does not separate and sequester each of the phases, it has a fundamental disadvantage compared with active samplers, which do. Compared to active air samplers, PAS will also inevitably give higher LODs and LOQs because of the smaller sampling volumes. With typical deployment periods of PAS between three months and one year and

sampling volumes of 0.5-4 m<sup>3</sup>/d, the total sampling volume will be in the order of a few hundred m<sup>3</sup>, a volume that an active sampler will collect within a few days.

In the UNEP GMP guidelines, active and passive samplers are recommended with typically one sampler deployed per sampling site. Existing POPs monitoring programs on a regional scale, such as MONARPOP<sup>4</sup>, UNECE-EMEP<sup>5</sup>, OSPAR-CAMP<sup>6</sup>, GAPS<sup>7</sup>, IADN<sup>8</sup>, have used active or passive samplers, sometimes combinations of both at the same site. However, there are not too many programs that include all twelve POPs as is envisaged in the GMP. The reason is the complexity of the analysis (*e.g.*, toxaphene) and the exceptionally low levels (*e.g.*, PCDD/PCDF). In those monitoring programs, typically concentrations for aldrin, endrin, heptachlor, and toxaphene (with some exceptions around Great Lakes) are close to or below the established limit of quantifications (LOQ) (see also Figure 1). Also in long-term exposed passive sampling devices low levels of POPs close to the LOQ are often found. On the other hand, other pesticides, such as endosulfan and hexachlorocyclohexanes (HCH), are typically observed at higher concentrations than the 12 initial Stockholm POPs. In addition, “new POPs” like brominated flame retardants, chlorinated paraffins and perfluorinated alkylated substances (PFAS) are found in substantial amounts in background atmospheric samples.

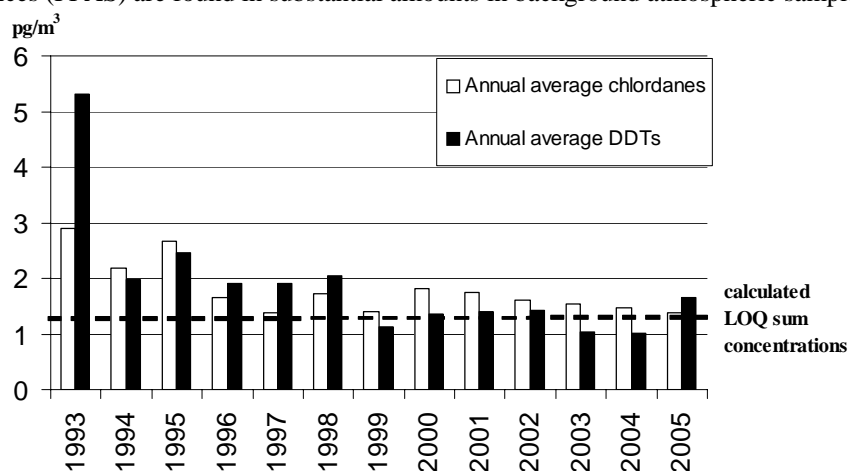


Figure 1: Annual average concentration (1993–2005) of  $\Sigma$ chlordanes and  $\Sigma$ DDT for the Zeppelin atmospheric monitoring station (Ny-Ålesund, Svalbard, Norway)<sup>9</sup> Sum chlordanes: *trans*-/*cis*-chlordane, *trans*-/*cis*-nonachlor; Sum DDT: *o,p'*-/*p,p'*-DDT, DDD, DDE.

Possible solutions to increase the number of quantifiable POPs in PAS include deployment of more than one sampler per site or extended exposure times. However, multiple samplers will not necessarily lower the detection limits if they are limited by blank levels, because those blank levels will likely increase when multiple samplers are combined. Longer exposure periods help decrease the detection limits if the uptake of the POPs into the PAS sorbent is kinetically (*i.e.*, by the rate of uptake, which is the case for most POPs) limited rather than thermodynamically (*i.e.*, by uptake capacity, which is the case for the more volatile POPs in the PUF-based samplers) limited. The latter is often the case for the more volatile POPs in the PUF-based PAS however this is being remedied by increasing the sorptive capacity of PUF-based PAS by impregnating them with XAD powder<sup>10</sup>. It should also be noted that longer exposure times are reducing the time resolution and thus limit the number of samples collected during one year, which may or may not be advantageous.

Active air samples generally have large sampling volumes, and they can be further increased by increasing the sampling time or the dimensions of the sampler (*e.g.*, NCP<sup>11</sup>). Whereas for the less volatile POPs longer exposure times may lead to better detection limits, the likelihood that POPs of higher volatility and/or air concentrations would experience break-through increases. Larger sampling volumes without the risk of increasing breakthrough can be achieved by parallel sampling and unification of sampling extracts but as discussed previously for PAS, detection limits will not necessarily decrease if they are limited by blank levels. Considering the quite large differences in the physical chemical properties (*i.e.*, vapour pressure/Henry's

constant and atmospheric half live) of the twelve POPs, it may be advisable to group the POPs into higher volatility POPs and lower volatility POPs and apply different sampling times for each group. Further reductions in LOQ may be achieved by modern detection methods (e.g., GC/MS-MS) that allow the elimination of noise and interferences.

## Discussion

Based on the above findings, it can be concluded that substantial efforts would be needed to quantify all or even the majority of POPs, in ambient air globally. These efforts are highly demanding on infrastructure and could, for example, include the use of more than one active sampler per site and the analysis of all POPs by HRMS and/or MS-MS. However, even with significant investment, such as multiple active samplers at one site and use of HRMS for identification and quantification, it cannot be assured that quantifiable concentrations would be found in all parts of the world.

Article 1 of the Stockholm Convention states the objective of the Convention “to protect human health and the environment from persistent organic pollutants”. The Convention calls for the reduction or elimination of releases of POPs, which should translate into reduced environmental levels over time and/or an assurance that environmental concentrations do not increase with time. The above mentioned findings have consequences for the design of the GMP and the interpretation of the data. With baseline concentrations below, or close to, the current levels of detection for at least some POPs, it may not be possible, in the near future, to establish time trends or spatial trends as envisaged in the quantitative evaluation of the global data. It could make sense to reduce the emphasis on those POPs that are routinely not detected (in a specific region), especially if this would result in a substantial resource or cost savings. However, these POPs should be reported as below some concentration (based on the limit of quantification) and periodically checked to ensure that levels do not increase in the environment.

## References

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