



Stockholm Convention on Persistent Organic Pollutants

**Conference of the Parties to the Stockholm
Convention on Persistent Organic Pollutants
Sixth meeting**
Geneva, 28 April–10 May 2013
Item 5 (i) of the provisional agenda*

**Matters related to the implementation of the
Convention: effectiveness evaluation**

Guidance on the global monitoring plan for persistent organic pollutants

Note by the Secretariat

1. As referred to in document UNEP/POPS/COP.6/28 on the global monitoring plan for effectiveness evaluation, the Secretariat has continued to support the process of revising and updating the guidance on the global monitoring plan for the evaluation of the effectiveness of the Convention and the work of the regional organization groups and the global coordination group for the global monitoring plan.
2. At their meeting, held in Geneva from 10 to 12 October 2012, the global coordination group and regional organization groups for the global monitoring plan further updated the guidance document to include additional technical information on the newly listed persistent organic pollutants, such as sampling and analytical methods, a correlation study for perfluorooctane sulfonic acid in human milk and serum, and environmental specimen banking aspects.¹ The updated guidance document on the global monitoring plan for persistent organic pollutants is set out in the annex to the present note; it has not been formally edited.
3. In addition, the Secretariat, in consultation with the global coordination group, made non-substantive changes to the global monitoring plan for persistent organic pollutants (UNEP/POPS/COP.6/INF/31/Add.1) and to the implementation plan for the global monitoring plan for persistent organic pollutants (UNEP/POPS/COP.6/INF/31/Add.2).

* UNEP/POPS/COP.6/1.

¹ The report of the meeting is set out in document UNEP/POPS/COP.6/INF/32.

Annex



GUIDANCE ON THE GLOBAL MONITORING PLAN FOR PERSISTENT ORGANIC POLLUTANTS

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DISCLAIMER

The designations employed and the presentations in this volume are possible options, based on expert judgment, for the purpose of providing comparable POPs monitoring data for the effectiveness evaluation of the Stockholm Convention. UNEP or contributory organizations cannot be liable for misuse of the information contained in it.

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LIST OF ABBREVIATIONS AND GLOSSARY OF TERMS

List of abbreviations

AMAP	Arctic Monitoring and Assessment Programme
ANCOVA	Analysis of Covariance
ANOVA	Analysis of Variance
BCF	Bioconcentration Factor
CEEPOPsCTR	Central and Eastern European Centre for Persistent Organic Pollutants
CEP	Caspian Environment Programme
CITES	Conference on International Trade in Endangered Species
COP	Conference of the Parties (to a Convention)
CRM	Certified Reference Material
CTD	The characteristic travel distance– defined as the “half-distance” (analogous to a half-life) for a substance present in a mobile phase
CV	Coefficient of Variation
DDD	Metabolite of DDT
DDE	Metabolite of DDT
ECD	Electron capture detector
ECEH	European Centre for Environment and Health
EMEP	Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe
EPA	Environmental Protection Agency
FAO	Food and Agriculture Organisation of the United Nations
GAPS	Global Atmospheric Passive Sampling Survey
GAW	Global Atmosphere Watch
GC	Gas chromatography
GEF	Global Environment Fund
GEMS	Global Environment Monitoring System
GMP	Global Monitoring Plan
GPC	Gel permeation chromatography
GPS	Global positioning system
HELCOM	Helsinki Commission/The Baltic Marine Environment Protection Commission
HPLC	High performance liquid chromatography
HRGC	High resolution gas chromatography (capillary column)
HRMS	High resolution mass spectrometer
I L	Instrumentation level
IADN	Integrated Atmospheric Deposition Network
ICES	International Council for the Exploration of the Sea
IMO	International Maritime Organisation
INSPQ	Centre de Toxicologie du Québec
IP/RP	International/regional programmes

IPCS	International Programme on Chemical Safety
JECFA	Joint FAO/WHO Expert Committee on Food Additives
LOD	Limit of detection
LOQ	Limit of quantification
LRM	Laboratory Reference Material
LRMS	Low resolution mass spectrometer
LRTAP	Long Range Transboundary Air Pollution Convention (under the auspices of UNECE)
LRTP	Long-range transport potential
MDL	Method detection limit
ML	Mililiter
MONARPOP	Monitoring Network in the Alpine Region for Persistent Organic pollutants
MS	Mass selective detector
NGOs	Non-governmental organisations
OC	Organochlorine
OCP	Organochlorine pesticide
OECD	Organisation for Economic Co-operation and Development
OSPAR	Oslo Paris Commissions, Convention for the Protection of the Marine Environment of the North East Atlantic
PCB	Polychlorinated biphenyls
PCDD	Polychlorinated dibenzo- <i>para</i> -dioxins
PCDF	Polychlorinated dibenzofurans
POPs	Persistent organic pollutants
PRTRs	Pollutant release and transfer registers
PTS	Persistent toxic substances
PUF	Polyurethane foam
QA/QC	Quality assurance and quality control regimes
ROGs	Regional organization groups for the Global Monitoring Plan
SMOC	The Sound Management of Chemicals (SMOC) initiative under the North American Agreement on Environmental Cooperation (NAAEC)
SOP	Standard operating procedure
TCDD	Tetrachlorodibenzo- <i>para</i> -dioxin
TEF	Toxic equivalency factor
TEQ	Toxicity equivalents
UNECE	United Nations Economic Commission for Europe
UNEP	United Nations Environment Programme
WHO	World Health Organisation
WMO	World Meteorological Organization
XAD	Styrene/divinylbenzene-co-polymer resin

Glossary of terms

Activity	Any programme or other activity or project that generates data or information on the levels of POPs in the environment or in humans that can contribute to the effectiveness evaluation under Article 16 of the Stockholm Convention
Core matrices	These are the matrices identified by the Conference of the Parties to the Stockholm Convention at its second meeting as core for the first evaluation: A = ambient air; M = (human) mother's milk; B = human blood
CTD	The characteristic travel distance– defined as the “half-distance” for a substance present in a mobile phase
I L-1	Instrumentation level ² capable to analyze PCDD/PCDF and dioxin-like PCB at ultra-trace concentrations (high-resolution mass spectrometer in combination with a capillary column)
I L-2	Instrumentation level capable to analyze all POPs (capillary column and a mass-selective detector)
I L-3	Instrumentation level capable to analyze all POPs without PCDD/PCDF and dioxin like PCB (capillary column and an electron capture detector)
I L-4	Instrumentation level not capable to do congener-specific PCB analysis (no capillary column, no electron capture detector or mass selective detector)
Intercomparisons	Participation in national and international intercalibration activities such as ring-tests, laboratory performance testing schemes, etc.
LOD	Limit of detection. Definition: The lowest concentration at which a compound can be detected; it is defined as that corresponding to a signal three times the noise
<LOD	Result below the of limit detection
LOQ	Limit of quantification. Definition: The lowest concentration that can quantitatively be determined is three times higher than LOD.
<LOQ	Result below limit of quantification. Compounds found at levels between LOD and LOQ can be reported as present, or possibly as being present at an estimated concentration, but in the latter case the result has to be clearly marked as being below LOQ
MDL	Method detection limit. The MDL considers the whole method including sampling, sample treatment and instrumental analysis. It is determined by the background amounts on field blanks.
Phase I	Activities to support the Article 16 effectiveness evaluation that will be conducted by the Conference of the Parties at its fourth meeting, information collected between 2000 and 2007 (also termed as first evaluation)
Phase II	Activities to support the Article 16 effectiveness evaluation after 2009
Programme	Some institutionalized activity to conduct measurements on a repetitive basis according to some agreed design, including the prospect for provision of necessary funding over a period of time
Selected Matrices	B = human blood; A = ambient air; BV = bivalves; BE = birds eggs; P 0 = fish; MM = marine mammals; W = water, S = soil; SD = sediments; F = food; and V = vegetation

² In this document, the term **Instrumentation level** is replacing the term **Tiers**, used in UNEP/POPS/COP.2/INF/10

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NOTE: Standard operation procedures and protocols contained in annexes 3-5 were valid at the time of publishing. They are attached in order to provide the reader with additional detailed information on various aspects of the POPs monitoring activities and the related QA/QC procedures. Web pages of the relevant institutions should be checked for possible updates before using the documents in the future.

1 BACKGROUND AND OBJECTIVES

The Stockholm Convention on Persistent Organic Pollutants (POPs) (UNEP, 2001) was adopted on 22 May 2001 and entered into force on 17 May 2004. As of December 2012 the Convention had 178 Parties.

The objective of the Stockholm Convention on POPs can be stated as to:

Protect human health and the environment from persistent organic pollutants by reducing or eliminating releases to the environment.

Parties have agreed that they need a mechanism to measure whether this objective is reached. According to Article 16 of the Convention, its effectiveness shall be evaluated starting four years after the date of entry into force of the Convention and periodically thereafter at intervals to be decided by the Conference of the Parties (COP). Each effectiveness evaluation will consist of three elements;

- Reports and other environmental monitoring information pursuant to paragraph 2 of Article 16;
- National reports submitted pursuant to Article 15 (*i.e.*, reports by Parties on the measures they have taken and the effectiveness of those measure); and
- Non-compliance information submitted pursuant to Article 17.

This guidance document is concerned only with the first of these elements, that is the development and implementation of arrangements to provide comparable monitoring information on the presence of the chemicals listed in Annexes A, B and C of the Convention, as well as their regional and global environmental transport.

The first edition of the guidance for the Global Monitoring Plan was developed and published in 2004, by UNEP Chemicals. Further to the second meeting of the Conference of the Parties to the Stockholm Convention, a Technical Working Group (TWG) was mandated to revise the original guidance document, in order to provide comprehensive technical guidance on all aspects of the implementation of the Global Monitoring Plan, including issues related to statistics, sampling, sample preparation, analytical methodology and data management (decision SC-2/13). At its third meeting the Conference of the Parties agreed that the Guidance on the global monitoring plan for POPs (GMP) provides an appropriate basis for the Parties to implement the global monitoring plan for persistent organic pollutants (decision SC-3/19, 2007).

The first GMP phase was successfully implemented and the first monitoring reports from all five UN regions and the Global monitoring report were presented at the fourth meeting of the Conference of the Parties in 2009. At this meeting, the Conference decided to add nine new chemicals to Annexes A, B and C of the Stockholm Convention (decisions SC-4/10-18). The Conference also mandated the global coordination group and the Stockholm Convention Secretariat to update the guidance document for the global monitoring plan³ with additional chapters on long-range transport and specimen banking, while also addressing the impact of listing new chemicals in the Convention (decision SC-4/31). Further chemicals are under investigation by the POPs Review Committee, including hexabromocyclododecane (HBCD) and short chain chlorinated paraffins (SCCP).

Revisions of the guidance document were undertaken by the global GMP coordination group supported by a group of experts specialized in the various document sections including experts who prepared the original document, organized and facilitated by the Stockholm Convention Secretariat. The expert group includes representatives of POPs monitoring programmes and experts with hands-on experience in sampling and analyzing POPs in various media, as well as representatives of regional organization groups for the GMP. Further experts were invited to provide targeted inputs, in particular representatives of ongoing POPs monitoring programmes such as AMAP, GAPS, RECETOX and WHO (the reference laboratory for the human milk survey).

1.1 The objectives of the POPs Global Monitoring Plan

To evaluate whether the levels of POPs were actually *reduced* or *eliminated* as requested by Articles 3 and 5 of the Convention, information on environmental levels of the chemicals listed in the annexes should enable detection of *trends* over time. Therefore focus is upon monitoring of background levels of POPs at locations not influenced by local sources. Reliable identification of trends will require that statistical evaluation is carried out on the design of each national monitoring programme contributing to the Global Monitoring Plan, to ensure that it is powerful enough to detect trends in time.

The objective of the POPs Global Monitoring Plan can therefore be described as to:

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 levels over time as well as to provide information on their regional and global environmental transport.

Reports on these activities form one of the components of information to be compiled by the global coordination group and the Secretariat to enable periodic effectiveness evaluations of the Convention by the Conference of the Parties.

1.2 The objectives of the guidance document

In order to meet the objectives of the Global Monitoring Plan, (*i.e.*, support the preparation of regional reports of comparable information on environmental background levels), the monitoring plan must provide guidance on, for example, how information is to be collected, analyzed, statistically treated, and reported. This guidance must also, in some cases, accommodate using existing programmes and in other cases the establishment of new activities. It must also describe a harmonized regime for the preparation of monitoring reports to support the periodic effectiveness evaluations to be undertaken by the Conference of the Parties.

The objective of the guidance document is therefore to:

Provide a uniform framework for all activities and tasks associated with collection, assessment and reporting of environmental background levels of the POPs listed in annexes A, B, and C of the Stockholm Convention in order to provide comparable information for the Conference of the Parties as required in paragraph 2 of Article 16 of the Convention.

This framework aims to assist programmes initiated specifically for the purposes of Article 16 and existing programmes that may wish to contribute to the Article 16 monitoring reports. In addition, the document is a key source of information for the comprehensive regional inventories of capacities together with the corresponding needs assessment, and the step by step capacity enhancement plan, that are to be prepared by the Secretariat at the request of the Conference of the Parties (SC-3/19). It also helps laboratories identified through the inventory building process in developing their capacity and in preparing targeted proposals for support from their government or from other donors. By its decision SC-4/31, the Conference of the Parties further requests the Secretariat to continue its support in training and capacity enhancement activities and assist countries in implementing the GMP for effectiveness evaluation.

The guidance document should be viewed as one part of an evolving set of documents that inform the reader about environmental information gathering and reporting methodologies to support effectiveness evaluation. In terms of increasing complexity, these documents include the following: Article 16 of the Convention; decisions of the Conference of the Parties, including decisions SC-2/13, SC-3/19 and SC-4/31; the Global Monitoring Plan and its implementation plan for the first evaluation; the guidance document, and media specific protocols on methodology.

The first edition of the guidance document was focused on the requirements to prepare for the first effectiveness evaluation. This second edition aims to address the impact of listing new POPs under the Convention by proposing adequate sampling methodologies for all compounds added in the Convention. The guidance is therefore intended to be a living framework, that is, one that may evolve and be elaborated over time to reflect further direction from the Conference of the Parties, experience gained and emerging specific needs. The present edition draws on the Global Monitoring Plan and the implementation plan for the first evaluation prepared by the Technical Working Group as amended by

the Conference of the Parties at its fourth meeting (decision SC-4/31). The most recent versions of these documents are available at <http://www.pops.int>

1.3 General principles

The framework developed by the Technical Working Group for the Global Monitoring Plan closely follows the direction given by the Conference of the Parties in decisions SC-2/13, SC-3/19 and SC-4/31. These decisions provide the general elements that should form the basis of the Global Monitoring Plan.

The Global Monitoring Plan should:

- Outline a strategic and cost-effective approach and build on, but not be limited to, existing and scientifically sound human health and environmental monitoring programmes to the extent possible, with the aim of providing appropriate and sufficient comparable data for the effectiveness evaluation of the Convention;
- Be practical, feasible and sustainable;
- Be inclusive, achieve global coverage and contain at least core representative data from all regions;
- Be designed to go beyond the first monitoring report and address long-term needs for attaining appropriate representative data in all regions;
- Provide for supplementing data, where necessary, taking into account the differences between regions and their capabilities to implement monitoring activities. Such progressive enhancement should be planned at the outset;
- Enable phased enhancement of the ability of parties to participate in regional arrangements for producing comparable data.

Substantial geographic differences currently exist in the availability of present monitoring capacity to contribute comparable data and information for the purpose of the effectiveness evaluation of the Stockholm Convention. A number of generic tasks to identify needs and opportunities to increase participation have been identified as follows:

- A comprehensive regional inventory of capacities should be developed and maintained and a corresponding needs assessment conducted by the Secretariat with contributions from national Stockholm Convention focal points;
- Capacity building for the purpose of implementing Article 16 should be guided by a plan for step-by-step capacity enhancement for Parties on a regional basis;
- Relevant regional centres could play a role in coordination efforts;
- A network of databases containing monitoring information should be developed and maintained.

The needs and opportunities for capacity-building to increase participation in the global monitoring plan are to be taken into account during the implementation of decision SC-4/22 on technical assistance.

In addition to the general principles of the Global Monitoring Plan a number of attributes of a cost effective monitoring framework, focused upon the needs of Article 16, have been identified as requiring particular emphasis. They are presented here because of their potential to assist in decision making in the regional and global context as the plan becomes operational:

- The plan should strive for simplicity and, to the extent possible, build on existing programmes to meet present and future needs. It should encourage plasticity, which is the ability to evolve over time in order to respond to the needs of the Convention while maintaining comparability. Plasticity is enhanced by simplicity of the original design.

- Clarity of design should be promoted for the sampling activities; of expectations for standards of analytical performance; and of arrangements for QA/QC.
- Differences in capacity within and between regions provide opportunities for regional capacity building focused to ensure a capability to detect regional trends. In order to put the GMP into regional reality, capacity building and sustainability will be a crucial aspect for implementation. Sustainability is strongly linked to both simplicity and effectiveness.
- Only the substances contained in Annexes A, B and C of the Convention are considered in the context of Article 16.
- It is essential to ensure inclusiveness and transparency in all aspects of the GMP design, conduct and reporting process without which there is a risk of lack of confidence and interest in the final reports.
- Monitoring for effectiveness evaluation (Article 16, paragraph 2) will not address: issues of compliance; preparation of dossiers for substances that may be proposed for addition to the Annexes of the Convention; hot spot detection and evaluation; or specific issues of scientific understanding.

1.4 Other information sources

The bases for the Global Monitoring Plan are: Article 16 of the Convention, decisions SC-2/13, SC-3/19 and SC-4/31; and the Global Monitoring Plan and the implementation plan for the first evaluation prepared by the Technical Working Group. The latter two documents will evolve over time and the reader can access the most recent versions at <http://www.pops.int>

In order to obtain an overview of laboratory capacity for POPs analysis worldwide, UNEP Chemicals maintains an inventory of POPs laboratories, which provides information on the technical and analytical capabilities of each laboratory so that potential partners for a POPs GMP may be identified. The title of the project is Assessment of Existing Capacity and Capacity Building Needs to Analyze POPs in Developing Countries and further information is available at: <http://www.chem.unep.ch/databank/Home/Welcome.aspx> and at: <http://www.chem.unep.ch/pops/laboratory/default.htm>

During the assessment process, the assessment teams should be able to use information derived from sources external to the GMP, providing that quality standards are not compromised. To assess the capacity of existing monitoring programmes, the Stockholm Convention Secretariat has opened discussions with organizations such as the World Health Organization, and other data producers and providers regarding access to information. When appropriate, memoranda of agreement with such organizations have or can be developed.

Article 11 of the Convention is concerned with the conduct of research and monitoring aimed to improve the basic understanding of such characteristics as the sources, movement, fate, behavior and toxicity of POPs in the environment. Those activities which can be conducted at any level of organization (*e.g.* national, regional or global) and are not restricted to the substances listed in the Convention are not formally linked to effectiveness evaluation. However it is possible that information resulting from such activity could be of assistance in the preparation of the Article 16 environmental reporting.

Article 16 does not specifically exclude non-parties from contributing information. Non-parties would be encouraged to contribute information and work that conforms to the framework described in this document, but would not be able to take part in decision making.

1.5 References

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Web references

Stockholm Convention on POPs <http://www.pops.int>

Ridding the world from POPs <http://www.pops.int/documents/guidance>

Assessment of Existing Capacity and Capacity Building Needs to Analyze POPs in Developing Countries
<http://www.chem.unep.ch/databank/Home/Welcome.aspx> and at:
<http://www.chem.unep.ch/pops/laboratory/default.htm>

GMP workshop, 2003 http://www.chem.unep.ch/gmn/Files/popsmonprg_proc.pdf

GEF/UNEP, 2000/3 http://www.chem.unep.ch/pts/gr/Global_Report.pdf

UNEP/POPS/INC.7/20 http://www.pops.int/documents/meetings/inc7/en/7_20.pdf

UNEP/POPS/INC.7/INF/15 http://www.pops.int/documents/meetings/inc7/en/7_15.pdf

UNEP/POPS/SC-2/13 http://www.pops.int/documents/meetings/cop_2/report/default.htm

UNEP/POPS/SC-2/9 http://www.pops.int/documents/meetings/cop_2/report/default.htm

UNEP/POPS/GMP-TWG <http://www.pops.int/documents/meetings/gmptwg/twg2/meetingdocs.htm>

2 SUBSTANCES TO BE MONITORED

2.1 Background

The objective of the Stockholm Convention is to protect human health and the environment from POPs with the ultimate goal to eliminate them, where feasible. An obvious way to evaluate the effectiveness of the Convention is to measure the concentration of the POPs listed in annexes A, B, and C of the Convention in relevant matrices (see Chapter 4). At the fourth meeting of the conference of the parties (COP-4) in May 2009, nine new persistent organic pollutants have been listed in addition to the initial twelve POPs, and at the fifth meeting of the conference of the parties (COP-5) in May 2011, one persistent organic pollutant has been additionally listed. Presently, the convention lists 22 POPs, which include the following substances or groups of substances:

1. Aldrin
2. Alpha-hexachlorocyclohexane (α -HCH) *
3. Beta-hexachlorocyclohexane (β -HCH) *
4. Chlordane
5. Chlordecone *
6. Dichlorodiphenyltrichloroethane (DDT)
7. Dieldrin
8. Endosulfan**
9. Endrin
10. Gamma-hexachlorocyclohexane (γ -HCH) *
11. Heptachlor
12. Hexabromobiphenyl (HBB) *
13. Hexabromodiphenyl ether and heptabromodiphenyl ether (PBDE)*
14. Hexachlorobenzene (HCB)
15. Mirex
16. Pentachlorobenzene (PeCBz) *
17. Perfluorooctane sulfonic acid (PFOS) *⁴
18. Polychlorinated biphenyls (PCB)
19. Polychlorinated dibenzo-*para*-dioxins (PCDD)
20. Polychlorinated dibenzofurans (PCDF)
21. Tetrabromodiphenyl ether and pentabromodiphenyl ether (PBDE)*
22. Toxaphene

Substances marked with an asterix were newly listed through decisions SC-4/10 through SC-4/18 at the fourth meeting of the Conference of the Parties in May 2009. Substances marked with two asterix were newly listed through decision SC-5/3 at the fifth meeting of the Conference of the Parties in May 2009.

The above list is restricted to the 22 POPs (status of 2011), but the COP may decide to add additional POPs to either of the three annexes, in which case these additional POPs would be included in the global monitoring programme and this chapter would have to be modified accordingly.

Table 2.1 gives an overview on the identity of the POPs, the number of congeners or structural isomers where the name of the POP represents a mixture.

4 As defined by decision SC-4/17 (precursors are included)

Table 2.1: Chemical identity of POPs including acronyms, number of congeners or structural isomers

POP	Acronym	Parent compound ⁵
Initial 12 POPs		
Aldrin		Single compound
Chlordane		2 isomers
Dichlorodiphenyltrichloroethane	DDT	2 isomers
Dieldrin		Single compound
Endrin		Single compound
Hexachlorobenzene	HCB	Single compound
Heptachlor		Single compound
Mirex		Single compound
Polychlorinated biphenyls	PCB	209 congeners
Polychlorinated dibenzo- <i>p</i> -dioxins	PCDD	75 congeners
Polychlorinated dibenzofurans	PCDF	135 congeners
Toxaphene		Technical mixtures of chlorinated bornanes and chlorinated camphenes (about 16,000 congeners or isomers)
POPs listed at COP-4		
Chlordecone		Single compound
alpha-Hexachlorocyclohexane	α -HCH	Single compound; isomer to β -HCH and γ -HCH
beta-Hexachlorocyclohexane	β -HCH	Single compound; isomer to α -HCH and γ -HCH
Lindane, gamma-Hexachlorocyclohexane	γ -HCH	Single compound; isomer to α -HCH and β -HCH
Hexabromobiphenyl	HBB	42 isomers in one homolog group
Pentachlorobenzene	PeCBz	Single compound
Tetrabromodiphenyl ether and pentabromodiphenyl ether (commercial pentabromodiphenyl ether)	c-penta BDE	Two homolog groups: 42 tetrabrominated isomers 46 pentabrominated isomers
Hexabromodiphenyl ether and heptabromodiphenyl ether (commercial octabromodiphenyl ether)	c-octa BDE	Two homolog groups: 42 hexabrominated isomers 24 heptabrominated isomers
Perfluorooctane sulfonic acid	PFOS	Single anionic compound with one linear and many branched isomers
POPs listed at COP-5		
Endosulfan		Single compound; mixture of stereoisomers

The following substances are under review by the POPs Review Committee (status 2011):

Candidate POPs under review (status 2011)		
	Acronym	Parent compound⁶
Hexabromocyclododecane	HBCD	3 structural isomers
Short-chain chlorinated paraffins (C ₁₀ -C ₁₃) alkanes	SCCP	Four homolog groups with varying degrees of chlorination; linear and branched isomers with skeleton either C ₁₀ , C ₁₁ , C ₁₂ or C ₁₃ ; (more than 6,000 isomers for Cl ₅ -Cl ₁₀)

2.2 Recommendations for POPs to be analyzed

Based on recommendations from the two workshops of the GMP Expert Group that considered the 2nd revision of the Guidance document for the GMP, held in April and September 2010 in Geneva (UNEP 2010) and because it may not be necessary or even possible to analyze all individual congeners of the mixtures in the above list, the following substances are recommended for analysis (see Table 2.2). Substances in Table 2.2 include the parent POPs but also some major transformation products that are covered under the Convention. In the case of PFOS, the decision SC-4/17 includes precursor compounds that are especially relevant for understanding long-range transport in air.

The POPs recommended for POPs analysis in global monitoring programmes are grouped according to core or recommended matrices. For the GMP, concentrations of POPs in various matrices have to be determined and changes in these concentrations need to be documented.

This is to be undertaken regionally while also achieving global coverage. Highest requirements on analytical performance are therefore needed to identify small changes in concentrations.

For the Global Monitoring Plan (GMP), it is recommended to collect data for all 22 POPs (parent compounds, precursor and transformation compounds as shown in Table 2.2 above) in recommended matrices (see chapter 4).

6 Theoretical number of congeners or structural isomers within this chemicals' group

Table 2.2: Recommended analytes and core matrices proposed for analysis
(Core matrices are air, human milk and human blood (all in bold); water is recommended to address the more water-soluble POPs such as PFOS)

	Compounds to be Monitored			
	Air	Human Milk	Human Blood	Water
Initial POPs				
Aldrin	Aldrin	Aldrin	Aldrin	Water has not been recommended as a core matrix for the lipophilic and nonpolar initial twelve POPs; therefore, analysis of surface waters is not recommended
Chlordane	<i>cis-</i> and <i>trans</i> -chlordane; and <i>cis-</i> and <i>trans</i> -nonachlor, oxychlordane	<i>cis-</i> and <i>trans</i> -chlordane; and <i>cis-</i> and <i>trans</i> -nonachlor, oxychlordane	<i>cis-</i> and <i>trans</i> -chlordane; and <i>cis-</i> and <i>trans</i> -nonachlor, oxychlordane	
DDT	4,4'-DDT, 2,4'-DDT and 4,4'-DDE, 2,4'-DDE, 4,4'-DDD, 2,4'-DDD	4,4'-DDT, 2,4'-DDT and 4,4'-DDE, 2,4'-DDE, 4,4'-DDD, 2,4'-DDD	4,4'-DDT, 2,4'-DDT and 4,4'-DDE, 2,4'-DDE, 4,4'-DDD, 2,4'-DDD	
Dieldrin	Dieldrin	Dieldrin	Dieldrin	
Endrin	Endrin	Endrin	Endrin	
HCB	HCB	HCB	HCB	
Heptachlor	Heptachlor and heptachlorepoxyde	Heptachlor and heptachlorepoxyde	Heptachlor and heptachlorepoxyde	
Mirex	Mirex	Mirex	Mirex	
PCB	ΣPCB ₆ (6 congeners): 28, 52, 101, 138, 153, and 180	ΣPCB ₆ (6 congeners): 28, 52, 101, 138, 153, and 180	ΣPCB ₆ (6 congeners): 28, 52, 101, 138, 153, and 180	
	PCB with TEFs* (12 congeners): 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189	PCB with TEFs* (12 congeners): 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189	PCB with TEFs* (12 congeners): 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189	
PCDD/PCDF	2,3,7,8-substituted PCD/PCDF (17 congeners)	2,3,7,8-substituted PCD/PCDF (17 congeners)	2,3,7,8-substituted PCD/PCDF (17 congeners)	
Toxaphene	Congeners P26, P50, P62	Congeners P26, P50, P62	Congeners P26, P50, P62	

* PCB with TEFs (Toxic Equivalency Factors) assigned by WHO in 1998

POPs listed at COP-4				
	Air	Human Milk	Human Blood	Water
Chlordecone	Chlordecone	Chlordecone	Chlordecone	
α -HCH	α -HCH	α -HCH	α -HCH	
β -HCH	β -HCH	β -HCH	β -HCH	
γ -HCH	γ -HCH	γ -HCH	γ -HCH	
Hexabromobiphenyl	PBB 153	PBB 153	PBB 153	
Pentachlorobenzene	PeCBz	PeCBz	PeCBz	
c-penta BDE	BDE 47, 99, 153, 154, 175/183 (co-eluting) Optional: BDE 17, 28, 100	BDE 47, 99, 153, 154, 175/183 (co-eluting) Optional: BDE 100	BDE 47, 99, 153, 154, 175/183 (co-eluting) Optional: BDE 100	
c-octa BDE				
PFOS ⁷	PFOS, PFOSA, NMeFOSA, NEtFOSA, NMeFOSE, NEtFOSE	PFOS, PFOSA	PFOS, PFOSA	PFOS, PFOSA
POPs listed at COP-5				
Endosulfan	α -, β -endosulfan; and endosulfan sulfate	α -, β -endosulfan; and endosulfan sulfate	α -, β -endosulfan; and endosulfan sulfate	

Perfluorooctane sulphonamide	PFOSA
N-methyl perfluorooctane sulfonamide	NMeFOSA
N-ethyl perfluorooctane sulfonamide	NEtFOSA
N-methyl perfluorooctane sulfonamidoethanol	NMeFOSE
N-ethyl perfluorooctane sulfonamidoethanol	NEtFOSE

From the substances under review, the following congeners and matrices are recommended for analysis to meet the objectives of the Global Monitoring Plan.

⁷ Referring to PFOS anion with linear and branched isomers

Candidate POPs under review (status 2011)				
	Air	Human Milk	Human Blood	Water
HBCD	α -HBCD, β -HBCD, γ -HBCD	α -HBCD, β -HBCD, γ -HBCD	α -HBCD, β -HBCD, γ -HBCD	α -HBCD, β -HBCD, γ -HBCD
SCCP (C ₁₀ -C ₁₃) alkanes	TBD	TBD	TBD	TBD

TBD: to be decided. Presently, the analytical methods still need further development before analytes can be recommended.

2.3 Recommended reporting format [

Spreadsheets to report the analytical data are available in EXCEL[®] format. These spreadsheets contain the individual analytes as shown in Table 2.2 and the sum parameters for groups or mixtures of POPs. Some recommendations on how to report the concentrations include the following:

For **PCB**, it is recommended to analyze and report the seven congeners individually to allow calculation of the sums of six or seven PCB depending on the monitoring program.

For the reporting of the **toxic equivalent (TEQ)** (for PCDD, PCDF, and dl-PCB) it is recommended to report the concentrations of all 29 congeners and separately show the TEQ derived from PCDD, PCDF and dl-PCB as well as the total TEQ. According to the text of the Stockholm Convention (annex C), the toxicity equivalency factors (TEF) as established by a WHO Expert Group and published in 1998 (WHO₁₉₉₈-TEFs) should be used. Further, the upper-bound (ND=LOQ) and the lower-bound (ND=0) values should be given. As a QA/QC measures, the difference between these two should be less than 20%.

For reporting the “sum of concentrations”, the mass concentrations of all the analytes including their transformation or precursor compounds should be added. However, since WHO and national food authorities report sum parameters of POPs in human tissues as equivalents of the parent POP, correction factors have to be applied for certain basic POPs. These sum parameters – called “POP_{give name of group/mixture equivalent}” should be reported as well to allow comparison with national reporting and literature data. The mathematical formulae are included in the EXCEL worksheet as well.

Detailed information on analysis and reporting of POPs concentrations can be found in chapter 5 and Annex 1 as well as in the chapters describing the matrices such as air, human matrices, and water.

2.4 References

Web references:

UNEP (2010): Report of the First Expert Meeting to update the Guidance on the Global Monitoring Plan for Persistent Organic Pollutants. Geneva, April 2010,
<http://chm.pops.int/Programmes/GlobalMonitoringPlan/hrMeetings/GMP1stExpertMeeting2010/tabid/760/mctl/VIEWDetails/EventModID/873/EventID/97/xmid/3258/language/en-US/Default.aspx>

UNEP (2010): Report of the Second Expert Meeting to update the Guidance on the Global Monitoring Plan for Persistent Organic Pollutants. Geneva, September 2010

PCB numbering and nomenclature:

Ballschmiter K. and Zell M. (1980): Analysis of Polychlorinated Biphenyls (PCBs) by Glass Capillary Gas Chromatography. Fresenius Z. Anal. Chem. 302, 20-31

K. Ballschmiter, R. Bacher, A. Mennel, R. Fischer, U. Riehle, and M. Swerev (1992). Determination of chlorinated biphenyls, chlorinated dibenzodioxins, and chlorinated dibenzofurans by GC-MS. J. High Resol. Chromatogr. 15:260-270.

Toxaphene numbering and nomenclature:

M. Coelhan and H. Parlar (1996): The nomenclature of chlorinated bornanes and camphenes relevant to toxaphene. Chemosphere 32, 217-228

Toxicity equivalency factors:

WHO re-evaluation (2005): http://www.who.int/ipcs/assessment/tef_update/en/index.html

3 STATISTICAL CONSIDERATIONS

The aim of this chapter is to review the statistical requisites that must be satisfied if a monitoring programme is to meet the objectives set out in Chapter 1. However, objectives at that level will not help to answer questions such as: *How many samples do we need to take? For how long a period do we need to continue monitoring? How frequent should we sample?* Furthermore, we need to specify the magnitude of the changes or differences we have to detect. The risks of reaching the wrong conclusions (e.g. to conclude that there is a trend when there is not or to miss a true trend) have also to be considered. The technical note to chapter 3 and associated case study provide further details on statistical considerations.

3.1 Quantitative objectives

Describing and carefully defining the objectives are the most crucial step in planning and organizing monitoring activities. It includes the choice of sampling matrices and strict definitions of sampling units and a description of what they represent in time and space. This description is a prerequisite for an appropriate interpretation of the results. However, in order to properly estimate, for example, the number of samples per sampling occasion, length of the time-series, sampling frequency etc., required for the investigation, quantitative objectives have to be defined. Quantitative objectives imply that the required sensitivity of the programme is stated, *i.e.* that the smallest change for temporal studies or smallest difference between areas for geographical studies is specified together with the required statistical power to detect such a difference at a specified significance level.

A quantified objective for temporal studies could thus, for example, be stated 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 %. (A 50 % decrease within a time period of 10 years corresponds to an annual decrease of about 7 %).

And for spatial studies, for example as follows:

To detect differences of a factor 2 between sites with a power of 80 % at a significance level of 5 %.

A significance level of 5% means that we are prepared to accept a risk of 5% to conclude from our data that there is a trend or difference when there actually is not. Similarly, a power of 80% means that we accept a risk of 20% to conclude that there is no trend or difference when it really is one. Statistical power and methods to estimate power are discussed in detail in Cohen (1988).

It had to be stressed, however, that statistically significant trends do not guarantee that detected temporal trends are a result of a causal relation between concentration and time. If the samples are biased, not comparable over time or if relevant confounding co-variants are not accounted for, “false-trends” may well occur.

Furthermore, in order to calculate, for example, the number of samples and the sampling frequency required to fulfil those objectives, an estimate of the sample variance is needed. Expected variance estimates could, perhaps, be extracted from similar ongoing monitoring programmes or, what is more reliable, be assessed from a pilot project using the same sampling strategy, sampling matrices etc. as the currently planned monitoring programme. In order to optimise the programme from a cost-benefit point of view, all costs, for example, for sampling, sample preparation and chemical analysis must be specified.

3.2 Representatives

It is essential that the suggested matrices are thoroughly described concerning what they represent in relation to contaminant load or exposure. Apart from factors like availability, sampling costs etc. information on, for example, concentration factors, bioaccumulation rates, metabolic capacity, and excretion rates would be useful. Various tissues within the same species vary considerably with respect to the above-mentioned factors *i.e.* they may represent totally different ranges of time and they may react to changes in the environment very differently.

Even though these questions are not purely interesting from a statistical point of view they will constitute invaluable pieces in the building of a modelling framework to enable an integrated assessment of contaminant load and exposure from various matrices.

Using mammals or species with a more or less developed capacity to degrade POPs may lead to spurious results. Elevated levels of one POP may trigger and enhance the metabolic capacity to degrade other POPs. This may cause a problem, for example, to evaluate spatial differences in POP exposure from human milk (Weiss *et al.*, 2003).

Monitoring contaminants on the global scale will inevitably raise question such as: *How many sampling sites do we need to appropriately represent a region?* Any firm advice from a statistical point of view needs estimates on spatial heterogeneity. For spatial studies the objectives have to be clearly specified (*e.g.* spatial trends, differences between regions etc.) and made quantitative. A variogram (Fig 3.1) may be used to describe the spatial correlation structure (Cressie, 1993; Davis, 1986). A sampling site does not represent a point outside the radius where the correlation with other stations ceases to exist better than any other sampling site outside this radius and thus hardly represent an area larger than an area confined by the perimeter of this radius.

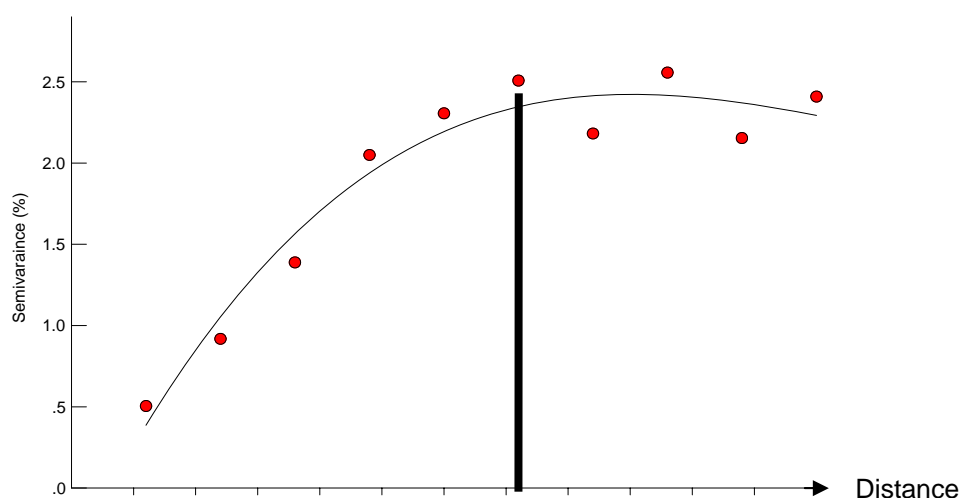


Figure 3.1: Showing an example of a variogram where the differences of concentrations between neighboring sites increases with distance up to a certain distance.

From a temporal trend perspective, a focus on well-defined strata of the monitored population/region will decrease the variance and improve the likelihood to detect changes over time.

When time-series are available from several sites within a region, statements about the presence or absence of trends in the same direction within the region are interesting. The homogeneity of trends can be checked using methods described in most standard text books in statistics (*e.g.* Dixon & Massey, 1969; Snedecor & Cochran, 1968). Van Belle and Hughes (1984) proposed a method for testing homogeneity among trends derived from the non-parametric Mann-Kendall trend test. Also methods from the fast growing field of meta-analysis can be of value when interpreting trends from several sites within and among regions (for example Hunter & Smith, 1990).

3.3 Sources of variation

There are numerous factors that affect measured concentration in environmental samples other than those of anthropogenic origin. For monitoring programmes that are designed to assess the effects of measures taken to reduce discharges of contaminants from industrial activities or control by means of pesticides, these factors can be considered as confounding factors. Avoiding or adjusting for confounders can improve statistical power in monitoring programmes considerably (Grimås *et al.*, 1985; Nicholson *et al.*, 1991b; Bignert, 2002).

Seasonal variation for several POPs (*e.g.* PCB, PCDD/PCDF, DDTs and HCB) has been demonstrated. The reasons could be both a seasonal variation in the discharge pattern from the sources and be due to, for example, physiological factors. If the main objective is to monitor the mean change in pollution load rather than to investigate the seasonal pattern in the discharges, sampling should be restricted to one season (the most favourable season from a minimum random variation point of view) in order to gain statistical power. The same arguments could be used if a diurnal pattern is discernible for fast changing matrices such as air.

Fat content and composition in human milk changes dramatically during the first weeks after birth, which leads to variation also in analysed POPs (*e.g.* Weiss *et al.*, 2003). In order to reduce random variation, sampling should preferably be carried out during a well defined period three weeks after birth (Also the fat content varies considerably depending on whether sampling is carried out in the beginning or at the end of the feeding session).

Other known or suspected confounding factors for which control is possible at sampling should be specified in the monitoring guidelines.

The use of narrow sampling unit definition implies that a smaller part of the studied population is represented. Often, this leads to unfounded assumptions of similar trends, for example, for both sexes or for various age classes. To improve representativity, if economy permits, stratified sampling should be applied rather than allowing for a wider definition of the sampling unit. General aspects of sampling design, applicable also for monitoring, are discussed, for example, by Underwood (1993, 1994, 1996).

The precision of chemical analysis is generally believed to constitute only a minor part of the total variance in monitoring time-series of environmental data where sample variation is expected to be large, much larger compared to laboratory precision. That is true if the same accredited laboratory is used through the whole series. However, if, from year to year, different laboratories carry out the analysis, it could seriously decrease or disable the possibility to evaluate time-series of, for example, POPs. The same is true if the same laboratory changes its methodology and, for example, co-elutions are resolved leading to a decrease in estimated concentrations unless measures are taken to compensate for them. If detection limits are improved, *i.e.* analytes are now found where they were not detected before, that may lead to similar problems depending on how results below the limit of quantification (LOQ) are treated. Further implications of concentrations below LOQ are discussed by Helsel (2006).

Provided that individual samples are taken and that appropriate confounding variables are registered or measured at the chemical analysis, the concentrations may be adjusted for varying covariates by means of, for example, ANCOVA (Analysis of Covariance). This may improve the power to detect changes over time or differences among sites considerably (Bignert, 2002). Furthermore, the detection and possible elimination of erroneous extreme values would also noticeably improve the power (Barnett and Lewis, 1994; Nicholson *et al.*, 1998; Bignert, 2002).

For temporal trends, the between-year variation may be expressed as the standard deviation of the residuals from a regression line on a log-scale or as a Coefficient of Variation (CV, %). The Coefficient of Variation found in time-series of contaminants in biological samples, including human milk, will most probably be over 35%, even if the between-year variation can be considered extremely low.

3.4 Length of time-series

It can be shown that several well-established monitoring programmes have surprisingly low power to detect temporal changes of significant importance (Nicholson and Fryer, 1991; Bignert *et al.*, 2004). It is naïve to expect monitoring time-series of POPs to reveal changes with any confidence within a sampling period of five years unless the changes are very large. More likely, we would expect a period

of at least 10-15 years to detect changes of moderate size (5 % /year). The relation between the number of years required detecting trends of various magnitudes and the Coefficient of Variation at a requested power of 80% is displayed in Figure 3.2.

A study would need at least 4-5 years of monitoring to give reliable estimates of random within- and between-years variation and other components of variance. This information would be invaluable for the improvement and fine-tuning of the on-going monitoring activity. It should be stressed that even for spatial studies a few years of sampling is not enough but can lead to spurious results (Bignert *et al.*, 1994).

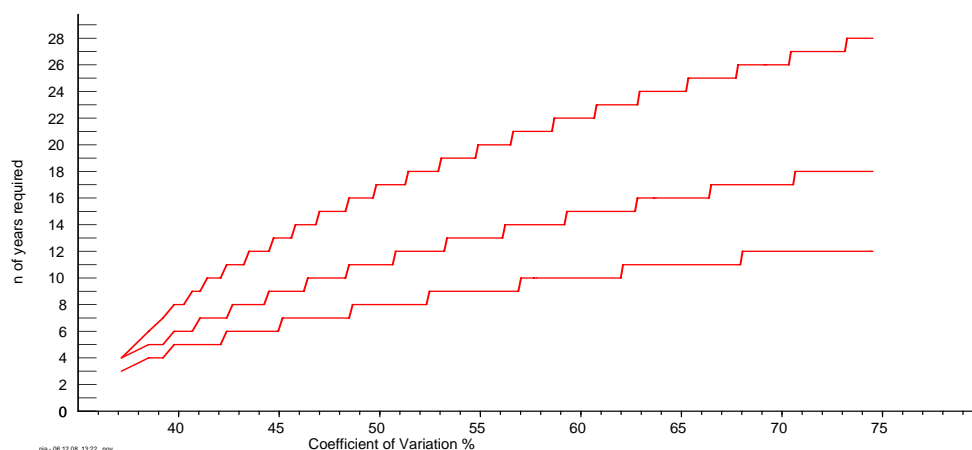


Figure 3.2: Number of years required to detect a 5 (left/above), 10 and 20% change per year respectively, at a power of 80% at a significant level of 5% applying a simple two-sided regression analysis for various magnitudes of between-years variation expressed as Coefficient of Variation (%) assuming single annual mean concentrations (or one pooled sample per year).

3.5 Number of samples needed

Larger samples provide more precise and reliable estimates of mean concentrations and variance. However, the contributions from additional samples depend to a very high degree on the sampling strategy.

To estimate the number of samples needed in an appropriate way for a certain situation, quantitative objectives must be defined and information on expected variance must be available (see above). The standard formulae for calculating the number of samples needed assume independent observations. In many typical monitoring situations this assumption is not altogether true. On a large scale, the weather situation one particular year at a sampling station may affect all the individual samples in the same direction.

Small-scale variation in time and space may not be covered by the sampling scheme which leads to an underestimated variance and increased between-year variation, for example, Bjerkeng (2000) showed that by sampling at three occasions during the sampling period instead of one and using the same number of samples or less, the yearly mean variance estimate could be reduced by up to 65%. Furthermore, stratified sampling and the choice between individual and pooled samples will affect the estimates of the required number of samples. Without the information mentioned above, no optimal figures on the required number of samples can be calculated.

Using pooled samples of several specimens will decrease the number of chemical analyses required to estimate a reliable mean concentrations compared to one or a few individual samples, since a larger proportion of the total population is represented. Disadvantages with pooled samples are that extreme values from single specimens may influence the concentration of the pool without being revealed, and that the possibility to adjust for confounding variables or correlate with biological effects disappears. Information on individual variance within a year has also a value in itself. An increased variance is often the first sign of elevated concentrations. In particular in the first stage of establishing a new sampling site, individual samples could help to reveal possible sources of variation. A more detailed discussion of advantages and disadvantages with individual versus pooled samples is given by Bignert *et al.* (1993).

3.6 Expected trends

Concentrations of pesticides can be expected to decrease relatively fast in environmental samples directly after a ban or other measures taken to reduce discharges, often with a magnitude of about 10 – 20 % per year. Similar trends have been measured in biota from terrestrial, freshwater and marine environments (Bignert *et al.*, 1998 a, b, c). That is, if a source disappears, the bio-available amount of hazardous persistent substances decreases much faster than that which may be expected from their estimated half-times. From a statistical point of view, this will enhance the possibilities to detect changes due to measures taken to reduce discharges, at least for persistent pesticides. For POPs such as PCB or others that are found in many different products in the techno-sphere the decrease would probably be lower, about 5-10 % per year. This means that the minimum trend possible to detect with a reasonable power (80%) should be smaller than 20% and preferably smaller than 10%. Assuming an appropriate sampling design, annual sampling for a period of ten years would probably be enough to detect trends in human milk/blood of 10% per year at a statistical power of 80% for pesticides and other POP's. Temporal trend analyses for air samples will preferably be treated with other methods (Chapter 4.1) that will affect the power calculation.

3.7 Expected sensitivity to detect trends

For a proper estimate of sensitivity, a pilot study should be carried out. It depends very much on the sampling strategy, choice of matrix, how well sampling follows the guidelines, whether the same laboratory is undertaking the analyses from year to year or not etc. The sensitivity will also differ between various POPs. For human milk the sensitivity could be expected to be, around 5% per year, assuming relatively large pooled (consisting of 25 individual samples) or individual samples of the same number following the guidance in Section 4.2. The power to detect a trend will depend of the magnitude of the change but also of course of the random between-year variation, these relations are illustrated in Figure 3.3. The sensitivity expressed as the minimum annual trend possible to detect, with a power of 80% during a sampling period of ten years as a function of the Coefficient of Variation is displayed in Figure 3.4.

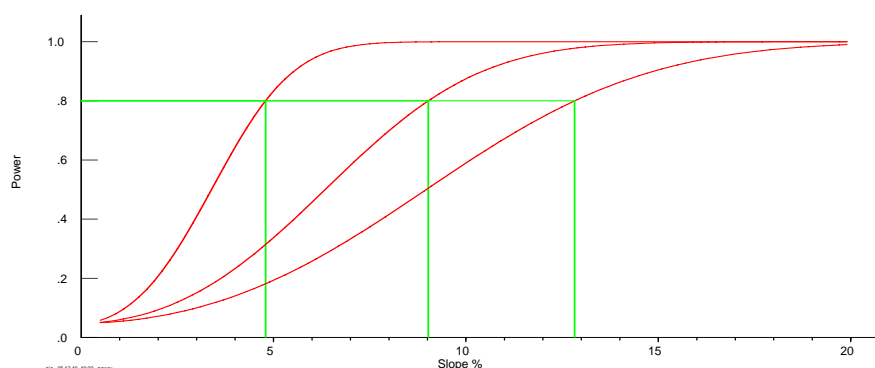


Figure 3.3: Power as a function of the minimum annual change possible to detect, after a sampling period of 12 years at a significant level of 5% applying a simple two-sided regression analysis for various magnitudes of between-years variation, expressed as Coefficient of Variation from left: 20, 40 and 60% respectively, assuming single annual mean concentrations (or one pooled sample per year).

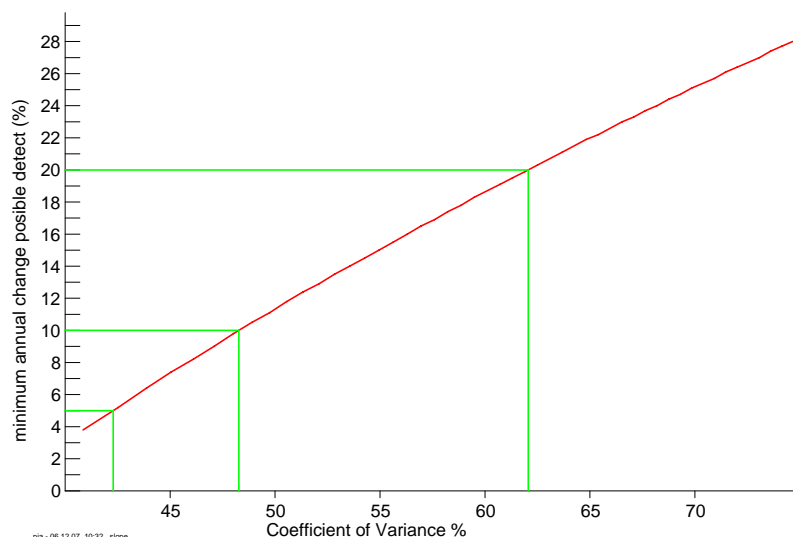


Figure 3.4: Minimum annual change possible to detect after a sampling period of 10 years at a power of 80%, a significant level of 5% applying a simple two-sided regression analysis for various magnitudes of between-years variation expressed as Coefficient of Variation (%) assuming single annual mean concentrations (or one pooled sample per year).

3.8 Sampling frequency for temporal trend studies

To determine an appropriate sampling frequency, the required temporal resolution has to be specified. To monitor certain events or incidents with a short time lapse, sampling may have to be carried out very often during certain periods. Considering, for example the half time for POPs in biological tissues, analytical cost etc., sampling once or, at most, twice per year is generally appropriate for monitoring of contaminants in biological samples. Sampling on several occasions during the sampling period to cover small scale temporal variation will, however, improve the mean estimate, as has been pointed out above). The examples above refer to sampling once a year. Obviously the statistical power of a trend-test is seriously reduced when sampling with a lower frequency.

If the length of a time-series is fixed, the power for various slopes at a certain between-year variation can be estimated. Figure 3.5 shows the relation between power and slope (e.g. the change in time-series of POPs measured in biota samples), estimated at sampling every, every-second, third and fourth year, respectively, at a standard deviation (between-year variation) along a regression line of 0.20 on a log-scale, corresponding to a Coefficient of Variation of 20-25%. If the desired sensitivity of the monitoring programme is to be able to detect an annual change of at least 5% per year within a time period of 12 years, the power is almost 80% for sampling each year at this standard deviation (Figure 3.5). For sampling every second, third or fourth year the corresponding power is only approximately 35, 17 and 10%, respectively.

3.9 Evaluation of results

Geographic information system (GIS) and modelling will inevitably play a great role in the interpretation and evaluation of the results for spatial distribution and exposure etc. It has to be stressed, however, that the reliability of such an evaluation will depend on the validation with real data from the environment and will become poor if the number of samples is too low. For time-series analyses a robust method proposed by Nicholson *et al.* (1995) has been used during recent years for several assessments of monitoring data within OSPAR, HELCOM and AMAP. This method supplemented with a non-parametric trend test and an efficient outlier test could form a basic package to evaluate temporal trends. Parametric tests are more powerful compared to non-parametric ones if the assumptions behind the tests are fulfilled (e.g. the residuals around the regression line is normally distributed). If however, this is not the case (e.g. if the presence of outlier violates the assumption of normally distributed residuals) the non-parametric tests become more powerful compared to the parametric ones.

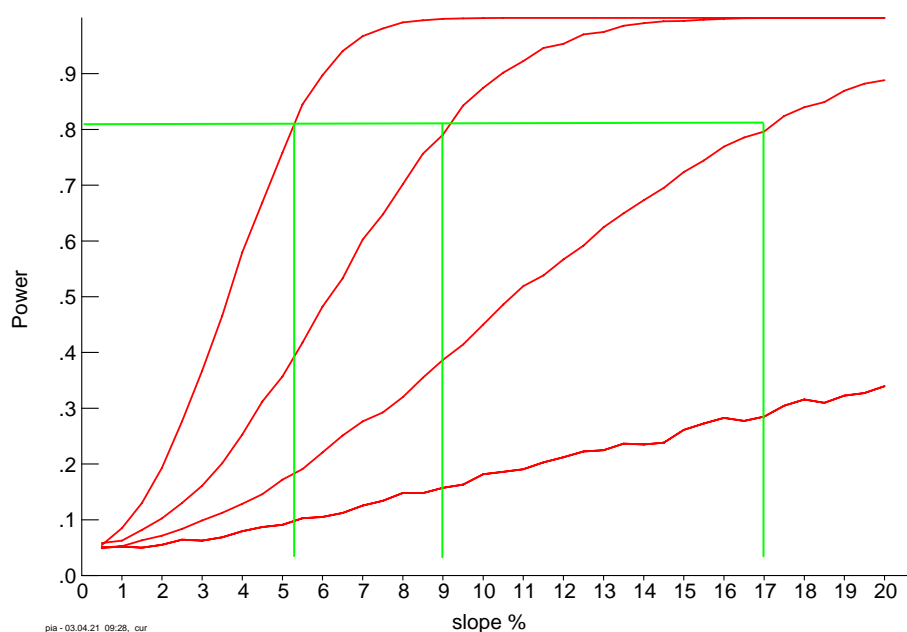


Figure 3.5: Power as a function of slope (annual change in %) at log-linear regression analysis (two-sided, $\alpha=0.05$) for a sampling period of 12 years at a residual standard deviation on a log-scale of 0.20, assuming normally distributed residuals. The graphs, from left to right, represent sampling every, every-second, third and fourth year, respectively and is based on Monte Carlo simulations at 10,000 runs.

3.10 Examples of statistical treatment and graphical presentation

One of the main purposes of the monitoring programme is to detect trends. Examples of methods to detect trends could be simple log-linear regression analyses. The slope of the line describes the yearly change in percent. A slope of 5 % implies that the concentration is halved in 14 years whereas 10 % corresponds to a similar reduction in 7 years and 2 % in 35 years.

The regression analysis presupposes, among other things, that the regression line provides a good description of the trend. The leverage effect of points in the end of the line is also a well-known fact. An exaggerated slope caused 'by chance' by a single or a few points in the end of the line, increases the risk of a false significant result when no real trend exists. A non-parametric alternative to the regression analysis is the Mann-Kendall trend test (Gilbert, 1987, Helsel and Hirsch, 1995, Swertz, 1995). This test has generally lower power than the regression analysis and does not take differences in magnitude of the concentrations into account, it only counts the number of consecutive years where the concentration increases or decreases compared with the year before. If the regression analysis yields a significant result but not the Mann-Kendall test, the explanation could be either that the latter test has lower power or that the influence of endpoints in the time-series has become unwarrantably great on the slope. Hence, the eighth line reports Kendall's 'tau' (see Table 3.1), and the corresponding p-value. The Kendall's 'tau' ranges from 0 to 1 like the traditional correlation coefficient 'r' but will generally be lower. 'Strong' linear correlations of 0.9 or above correspond to tau-values of about 0.7 or above (Helsel and Hirsch, 1995). This test has been recommended for use in water quality monitoring programmes with annual samples in an evaluation comparing several other trend tests (Loftis *et al.*, 1989).

In order to describe non-linear trend components in the development over time some kind of smoothed line could be applied. The smoother used in the example (Figure 3.6) is a simple 3-point running mean smoother fitted to the annual geometric mean values. In cases where the regression line is badly fitted the smoothed line may offer a more appropriate description. The significance of this line is tested by means of an ANOVA (Analysis of Variance) where the variance explained by the smoother and by the regression line is compared with the total variance. This procedure is used at assessments at ICES and is described by Nicholson *et al.*, 1995, see the smoothed line in the HCB-plot in the example (Figure 3.6).

Observations too far from the regression line considering what could be expected from the residual variance around the line is subjected to special concern. These deviations may be caused by an atypical occurrence of something in the physical environment, a changed pollution load or errors in the sampling or analytical procedure. The procedure to detect suspected outliers in this example is described by Hoaglin and Welsch (1978). It makes use of the *leverage coefficients* and the *standardised residuals*. The standardised residuals are tested against a $t_{.05}$ distribution with $n-2$ degrees of freedom. When calculating the i th standardised residual the current observation is left out implying that the i th observation does not influence the slope nor the variance around the regression line.

Some organic contaminant, herring muscle, s. Baltic Proper

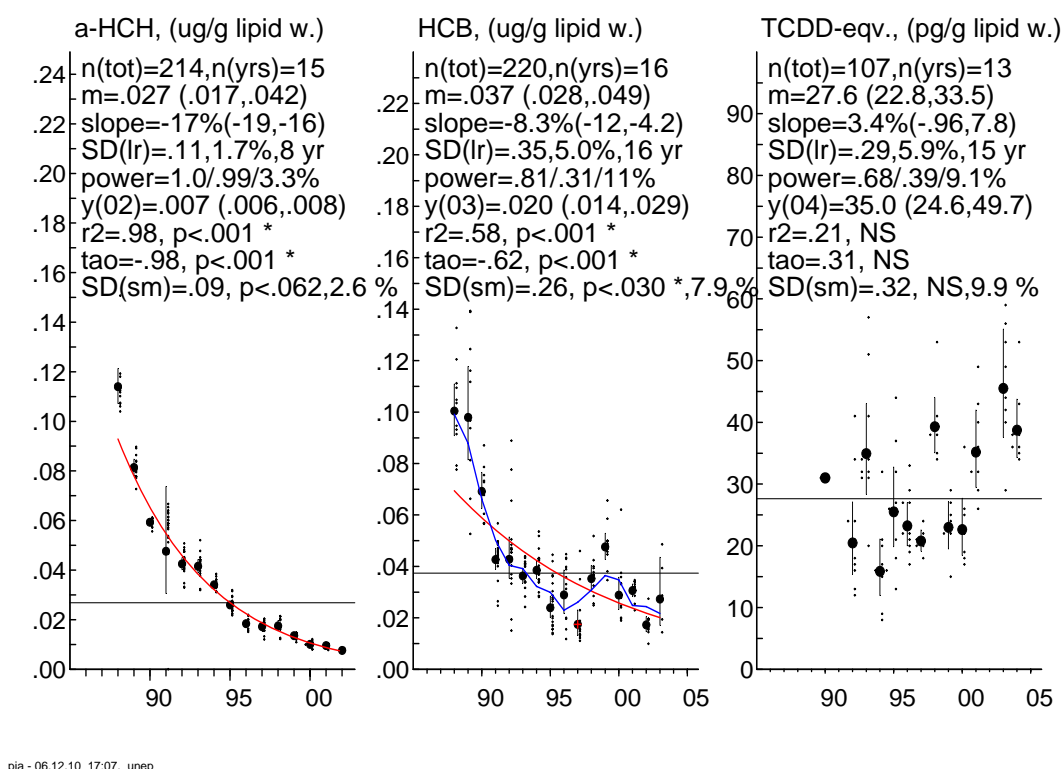


Figure 3.6: Examples of time-series; alpha-HCH, HCB and TCDD-equivalents ($\mu\text{g/g}$ lipid weight) in herring muscle from the southern Baltic Proper. The legend to the figure is found in Table 3.1.

Table 3.1: Legend to Figure 3.6

The plots display the geometric mean concentration of each year (circles) together with the individual analyses (small dots) and the 95% confidence intervals of the geometric means. The overall geometric mean value for the time-series is depicted as a horizontal, thin line. The trend is presented by a regression line (plotted if $p < 0.05$, two-sided regression analysis). The log-linear regression lines fitted through the geometric mean concentrations follow smooth exponential functions. A smoother is applied to test for non-linear trend components. The smoothed line is plotted if $p < 0.05$. Below the header of each plot the results from several statistical calculations are reported:

n(tot)= Total number of analyses included together with the number of years (**n(yrs)**=).

m= The overall geometric mean value together with its 95% confidence interval (N.B. the number of degrees of freedom = n of years - 1).

slope= The slope, expressed as the yearly change in percent together with its 95% confidence interval.

sd(lr)= The square root of the residual variance around the regression line, as a measure of between-year variation, together with the lowest detectable change in the current time-series with a power of 80%, one-sided test, $\alpha = 0.05$. The last figure is the estimated number of years required to detect an annual change of 5% with a power of 80%, one-sided test, $\alpha = 0.05$.

power= The power to detect a log-linear trend in the time-series (Nicholson and Fryer, 1991). The first figure represents the power to detect an annual change of 5% with the number of years in the current

time-series. The second figure is the power estimated as if the slope were 5% a year and the number of years were ten. The third figure is the lowest detectable change (given in percent per year) for a ten year period with the current between year variation at a power of 80%.

r²= The coefficient of determination (r^2) together with a p-value for a two-sided test (H_0 : slope = 0), i.e. a significant value is interpreted as a true change, provided that the assumptions of the regression analysis is fulfilled.

y(02)= The concentration estimated from the regression line for the last year together with a 95% confidence interval, e.g. $y(02)=0.007$ (0.006, 0.008) is the estimated concentration of year 2002 where the residual variance around the regression line is used to calculate the confidence interval. Provided that the regression line is relevant to describe the trend, the residual variance might be more appropriate than the within-year variance in this respect.

tau= The Kendall's 'tau' as a result from the non-parametric Mann-Kendal trend test, and the corresponding p-value.

sd(sm)= The square root of the residual variance around the smoothed line. The significance of this line could be tested by means of an Analysis of Variance. The p-value is reported for this test. A significant result will indicate a non-linear trend component.

3.11 References

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4 SAMPLING AND SAMPLING PREPARATION METHODOLOGY

The focus of the Global Monitoring Plan to support the effectiveness evaluation of the Stockholm Convention is on environmental background concentrations in media with a high potential for comparability. The Conference of Parties has decided that the air monitoring and human exposure through breast milk or maternal blood will be used as core media for the first evaluation. For future evaluations, the Conference of the Parties has also decided to supplement the core data with data from other media such as biota, water, soil, and sediments. The present guidance was revised to support future evaluations of the Convention, including consideration of supplemental media for future evaluations and specific considerations *e.g.* for sampling.

Some general considerations that pertain to all the GMP matrices are discussed below.

All sampling should follow established methodological guidelines, which should be agreed upon before the start of any programme activity in a region. If possible, samples in all programmes should be numbered in the same way. Sampling should always include field or trip blanks and, to the extent possible, duplicate samples for the purpose of sample sharing and the analysis of variance.

The sampling window for the initial baseline is 2003, plus or minus five years. Sample frequency and timing should, as much as possible, be harmonized between matrices. As a rule samples should be taken at least annually and during the same period every year. For some matrices where seasonal influences would be less important (*e.g.* human breast milk), the sampling frequency and duration might be different. For the statistical analysis of the levels it would be preferable to take many samples frequently from one location rather than to take a few samples from many different locations. Further guidance on number of samples is given in Chapter 3.

Sample banking should be considered for all samples. Sample banking is an expensive and resource intensive activity that needs to be sustainable in a long time perspective. However, if properly managed, it may yield important insights into exposures over time (*e.g.* for newly listed POPs) and may also be used for retrospective studies. Further guidance on environmental specimen banking is given in Chapter 8.

4.1 Air

The first global monitoring report of the Stockholm Convention on POPs was adopted by the Conference of the Parties in May 2009 and summarized information from existing air monitoring programs on POPs. This information established baseline levels or trends of POPs upon which future trends could be established. The ultimate goal of compiling monitoring data for air is to establish whether or not, and the extent to which, measures implemented to control POPs releases lead to declining concentrations in air, *i.e.* effectiveness of control measures. Air is an important receiving medium for POPs and for their transport and delivery to the broader environment.

The first global monitoring report revealed that most air data on POPs was contributed by a relatively small number of monitoring programmes and that the continuation of these programmes is essential (Fig. 4.1.1). The report also revealed that data on POPs levels in air was lacking in some regions and should be addressed through capacity strengthening efforts and the establishment of sustainable and coordinated air monitoring programmes.

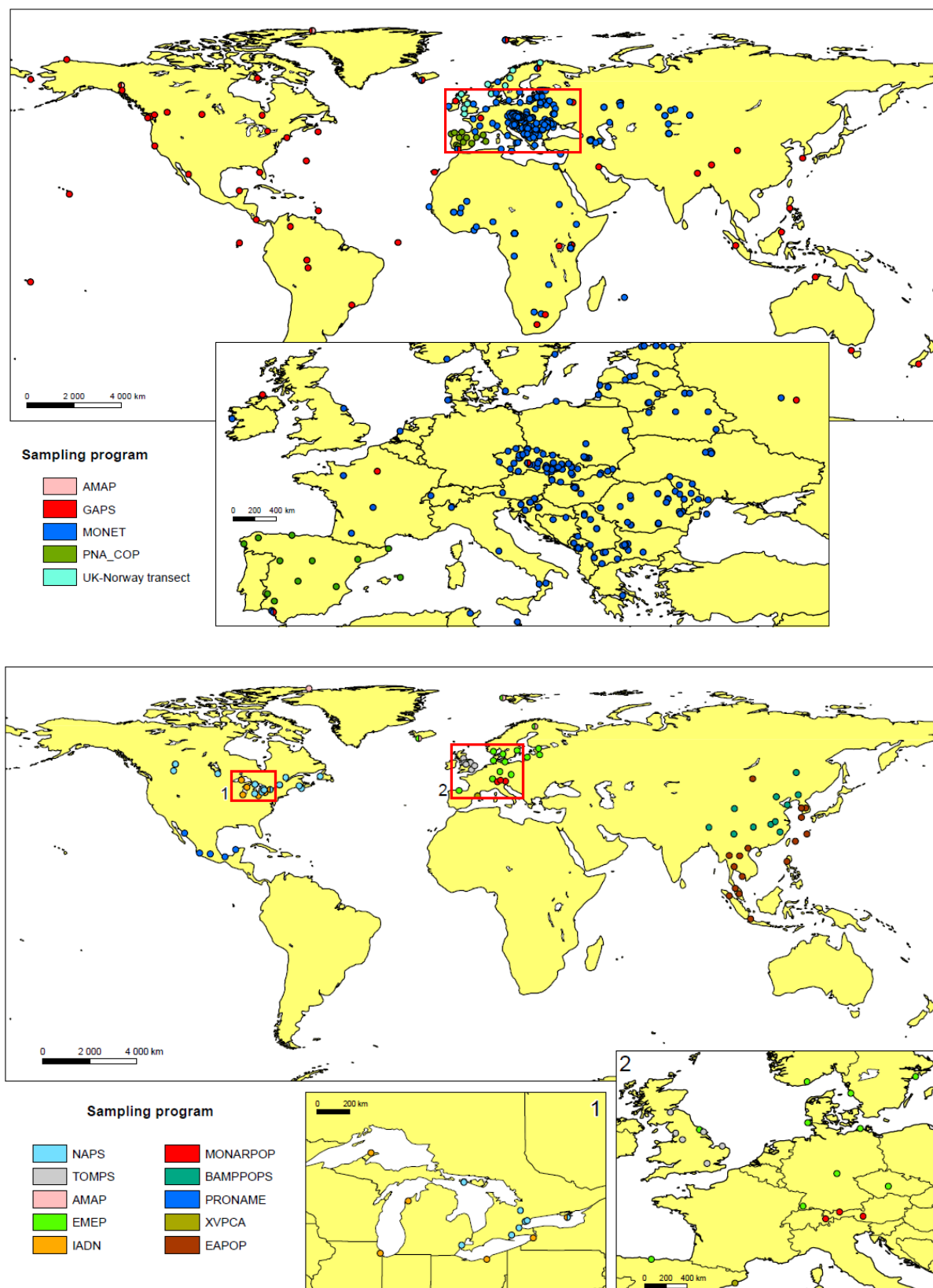


Figure 4.1.1: Sampling sites currently operating under existing air monitoring programmes for POPs that are contributing to the GMP. Top panel – passive sampling networks; bottom panel – high volume air sampling networks

Several key recommendations stem from the first global monitoring report and inform new and ongoing efforts to assess POPs in air for the purpose of effectiveness evaluation. These are summarized below and include, *inter alia*:

- i. A need to ensure internal consistency of data within programmes so that trends over time can be evaluated; at the same time, to strive for comparability of data among programmes so that data sets can be combined.
- ii. Consideration of long-range transport and climate effects on POPs when evaluating data on POPs in air.
- iii. Acknowledgement that in some locations, the response in air concentrations to control measures may be subject to a time lag due to the persistence of POPs.
- iv. Monitoring of newly listed POPs in air should be undertaken as soon as possible so that adequate baselines are established.
- v. The development of new and sustainable programmes for addressing data gaps for POPs in air should take advantage of partnerships with existing programmes; a specimen banking strategy should also be considered (*i.e.* collection and archiving of air samples for later analysis) if current analytical capacity is an issue.

This guidance chapter for air has been revised to reflect these new challenges. The second global monitoring report will be submitted at the seventh meeting of the Conference of the Parties in 2015. This allows several years to develop new air monitoring programmes to address data gaps and interpret available data to assess temporal trends in air.

Some air monitoring programs have already started to investigate and report on some of the nine newly listed POPs and other POP-like chemicals of interest in air (Muir and de Wit, 2010; Genualdi et al., 2010, Martrat et al., 2012). These studies can provide additional useful information and guidance on sampling and analytical challenges.

4.1.1 Experimental design

Sampling sites

The objective of the ambient air sampling network is to obtain representative data for assessing baselines and changes over time and space and the regional and global transport of POPs. We interpret 'representative' as being a sufficient number of sampling sites to make general conclusions about POPs trends and not to be representative of heterogeneity of that region. Chapter 3 (Statistical considerations) shows that complete geographical coverage for a particular region or continent is not economically feasible and would require an extremely dense sampling network and considerable prior investigatory work to assess regional variability on air concentrations in POPs.

Initially, for addressing POPs trends, the GMP should in each region strive for at least:

- Three to five stations with active high-volume sampling;
- A network of 10 to 15 passive sampling stations arranged in a grid with spacing of approximately $20^{\circ} \times 20^{\circ}$ for enhancing geographical coverage⁸. Passive samplers should be co-located at the high volume sites for comparison purposes.

These sites may be located centrally so as to obtain information on time trends of regional sources. The sites should avoid individual and large sources of POPs so that they reflect a large area around the site (*e.g.* 100 km) and not emissions from just a few local point sources. Requirements for such a site include the availability of meteorological observations and station personnel who could be trained in the sampling techniques. Regional decision on site selection might also include geographic considerations and use should be made of existing air quality monitoring sites that meet the appropriate site selection criteria, such as those operated by members of the World Meteorological Organization (WMO) under the Global Atmosphere Watch (GAW) programme.

This network may be supplemented by additional passive sampling sites situated on islands and on continental margins to yield information for addressing transcontinental transport between regions.

In summary, two types of measurements of a full range of POPs are envisioned in each region:

⁸ Also other techniques / technologies providing comparable data could be considered

- **Cumulative sampling** (for 1 to 2 days every week or continuously over periods of 1 to 2 weeks) by active high volume sampling ($\sim 0.5\text{--}1\text{ m}^3/\text{min}$. flow rate) at a few sites in each region. These samples would be separated into particulate and gaseous fractions; and
- **Continuous, cumulative passive (diffusive) sampling** for integration periods of 3 months to 1 year using passive samplers deployed at a large number of sites, including the high volume sampling sites.

Examples of protocols, standard operating procedures and detailed guidance on sampling, sample treatment and analysis are provided in Annex 5 (attached only to the electronic version of the guidance).

Siting considerations

The combination of a number of long-term active sampling sites supplemented by a larger number of passive sampling sites will yield a cost-effective programme with flexibility to address a variety of issues. Regional availability of laboratories and consideration of sources and air transport pathways will influence the spatial configuration and density of the network.

It is important to encourage co-operation between countries within regions and consultation with POPs modellers to ensure that the best sites are selected, and that observational practices are standardized. Available facilities at which other atmospheric composition measurements are made should be used whenever possible or feasible.

Positioning and installation of samplers should follow standard operating procedures for air sampling programs. A detailed description of all selected sites should be provided. More general criteria are given here:

- **Regional representativity:** A location free of local influences of POPs and other pollution sources such that air sampled is representative of a much larger region around the site.
- **Minimal meso-scale meteorological circulation influences:** Free of strong systematic diurnal variations in local circulation imposed by topography (*e.g.* upslope/ down slope mountain winds; coastal land breeze/lake breeze circulation).
- **Long term stability:** In many aspects including infrastructure, institutional commitment, land development in the surrounding area.
- **Ancillary measurements:** For the super-sites, other atmospheric composition measurements and meteorological wind speed, temperature and humidity and a measure of boundary layer stability. For the passive sites, meteorological wind speed, temperature and humidity.
- **Appropriate infrastructure and utilities:** Electrical power (for pumped samplers), accessibility, buildings, platforms, towers and roads.

Site description should follow a standardized approach and should be documented with additional information such as digital photos of the sampling location and the surrounding region and a detailed description of the surrounding area including identification of suspected or potential point sources (including approximate location relative to the sampling site). The following two-step site characterization procedure is recommended that provides information on: 1) the site type and 2) potential source inputs for POPs at the site. It should be emphasized again that sites should be chosen that are not influenced directly by just a few nearby sources, to ensure that they are representative or characteristic of a larger region.

Site type:

- ☐ urban
- ☐ sub-urban
- ☐ rural
- ☐ remote
- ☐ high altitude
- ☐ polar

Potential Source type (more than one type is possible):

- ☐ industrial
- ☐ traffic
- ☐ residential
- ☐ agricultural
- ☐ waste sector
- ☐ none, *i.e.* continental background site

□ marine/coastal

Note: population density can be used as an approximate guide for site classification as follows:

urban = >200 000 inhabitants within a 10 km radius.

sub-urban = between 20 000 and 200 000 inhabitants within a 10 km radius

rural = between 2000 and 20 000 inhabitants within 10 km radius

remote = relatively uninhabited (<2000 inhabitants within a 10 km radius)

Site information and classification is important for comparing data within a region and among regions. Although new sampling networks should focus on sites that are representative of a large region or ‘footprint’ (*i.e.* rural sites), the establishment of sites in urban, industrial, and agricultural regions may be useful as ‘context sites’ for comparison purposes. For regions that are relatively pristine for some POPs, the inclusion of context sites will also improve detection and reporting of POPs. Again, care should be taken to ensure that these ‘context sites’ are not directly or heavily influenced by just a few nearby point sources.

The approach described above provides a qualitative description of the sampling site. This information will be helpful at the data storage stage as many of the data bases for air have similar fields for describing and categorizing sites. The remoteness index concept, discussed in the next section, provides a quantitative measure for describing a site and its potential influence from agricultural or industrial sources of POPs. This quantification of potential source inputs for given sites may facilitate data interpretation and comparison of results from different sites. The index values can also inform site-selection at the onset of a study.

Characterization of transport to the sites

A better understanding of POPs concentrations and trends at a particular site may be obtained through an evaluation of regional and global scale transport pathways. To do this, an understanding of local (meso-scale) as well as large (synoptic) scale air transport pathways to the site is required. This is achieved through local meteorological measurements to characterize meso-scale influences as well as use of Lagrangian or Eulerian transport models to reconstruct the large scale transport pathways to the site. It is also important that for water-soluble POPs, oceanic and riverine transport and air-water exchange be considered, especially for sites located on coastlines.

As a first step, it may be useful and insightful to consider the long-range transport potential (LRTP) for the various POPs. The characteristic travel distance (CTD) – defined as the “half-distance” (analogous to a half-life) for a substance present in a mobile phase – is a useful parameter in this context. CTDs in air and water having been calculated using the OECD Tool, which considers various degradation and transport pathways that chemicals may undergo based on their physical-chemical properties (Wegman et al., 2009). CTDs for chemicals discharged into air and water are listed in Table 4.1.1. It is important to note that these distances should be compared in a relative manner and are dependent on model parameterizations (Stroebe et al., 2004). The transfer efficiencies (TE, %) for the selected POPs were also calculated for emissions to air. Transfer efficiency is defined as the rate of deposition of a pollutant to soil and water in a distant region divided by the rate of emission in a source region. Some POPs undergo several cycles of deposition and re-volatilization during their lifetime in the environment, therefore transfer efficiencies of greater than 100% are possible. A review of metrics for describing LRT of POPs is presented by Scheringer (2009).

Table 4.1.1: Characteristic travel distances (CTDs, km) for air and water and transport efficiencies (%) for selected POPs. (POPs are ranked highest to lowest in terms of the CTDs for air and calculations are performed at 25 °C). Calculations performed using OECD Tool*

Chemical	CTD (air)	CTD (water)	TE% (emission to air)
Hexachlorobenzene	230 000	700	2500
Pentachlorobenzene	120 000	200	50
Octabrominated Diphenyl ethers	22 000	360	110

PCB-180 (hepta homolog)	17 000	340	91
α -HCH	7800	830	54
PCB-28 (tri homolog)	5100	190	2.2
γ -HCH	4200	220	19
BDE-99	3700	540	15
DDT	3600	490	10
β -HCH	3100	430	3.7
Hexabromobiphenyl	3000	540	13
Toxaphene	2800	1600	7.9
Short-chain chlorinated paraffins	1800	230	0.78
2378-TCDD	1600	130	0.58
Dieldrin	1100	580	0.89
chlordanes	1100	300	0.46
chlordecone	710	1700	3.2
Aldrin	60	130	0.00018
PFOS**	10	63 000	0.049

TE – transfer efficiency for emissions to air; HCH – hexachlorocyclohexane; PCB-polychlorinated biphenyl; DDT – dichlorodiphenyltrichloroethane; TCDD – tetrachlorodibenzodioxin; PFOS – perfluorooctane sulfonate;

*Calculations using OECD Tool are summarized at: http://www.sust-chem.ethz.ch/docs/POP_Candidates_OECD_Tool.pdf

<http://www.pops.int/documents/meetings/poprc/prepdocs/annexEsubmissions/All%20chemicals%20Switzerland.pdf>

**calculation of CTD for air for PFOS assumed no potential to volatilize to air.

The resulting CTDs indicate that with the exception of PFOS and aldrin, most of the listed POPs are “flyers” and the atmospheric transport pathway is important. POPs for which the water transport pathway is significant (the “swimmers”) include: PFOS, chlordecone and toxaphene.

A common transport pathway analysis tool that can facilitate the detection and interpretation of trends in POPs air concentrations is based on air-parcel back-trajectory analysis. Services for generating air parcel trajectories for user defined locations are now available on-line and often free of charge (e.g. [www.noaa](http://www.noaa.gov) – Hysplit model; [www.particle-transport](http://www.particle-transport.com) model). In this approach, the transport path of air to a site during sampling is reconstructed from observed wind fields. There are various methodologies that have been applied to improve trend detection ranging from trajectory sector analysis to cluster analysis. In the latter, discriminate analysis is utilized to identify the main groups of trajectory pathways to a site (Moody et al., 1998). This can also be done for samples that fall in various percentile ranges of the trajectory distribution. Another approach that utilizes trajectories to identify sources and “preferred transport pathways” is potential source contribution function analysis (PSCF) pioneered for POPs by Hsu et al. (2003a and b). In this approach, upwind areas in a grid placed over the map are identified that are most frequently occupied by points in a three to five days back trajectory for high concentration versus low concentration percentile trajectories. Insight into upwind sources and trends in air transported from those regions that is gained from the above analyses is much more effective in addressing policy questions than simple time-series analysis of observations.

Gouin et al., (2005) demonstrated how density maps (a modification of the PSCF approach) could be used to interpret time-integrated, passive sampler-derived data (Fig. 4.1.2) by identifying an air shed associated with the history of the air mass transported to a particular site.

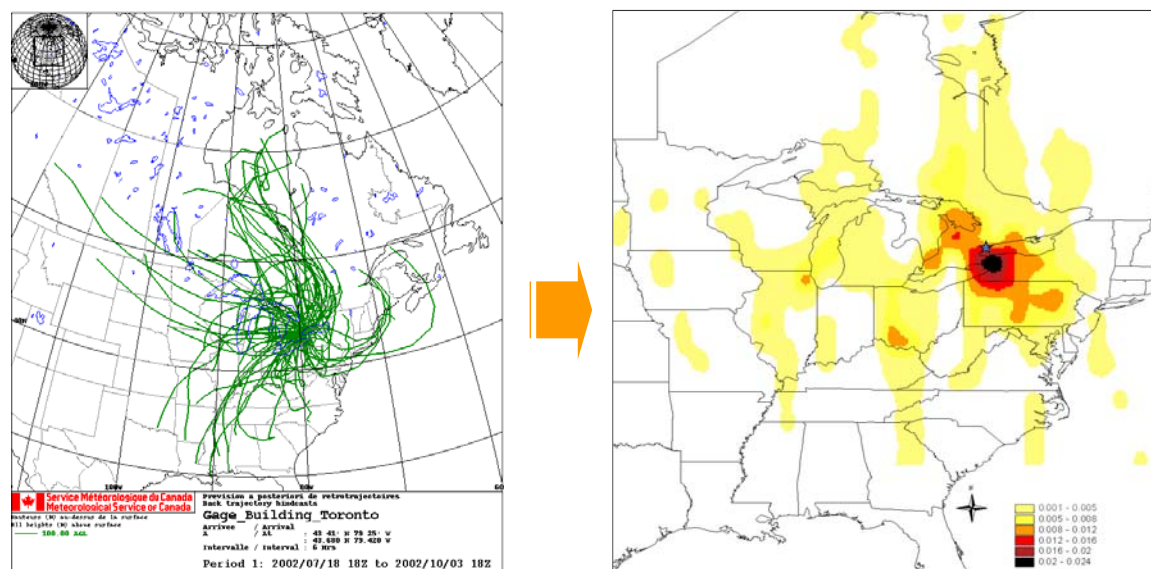


Figure 4.1.2: Example of probability density map (right panel) constructed from daily 3-day air parcel back trajectories for a time-integrated air sample. The darker shadings in the right panel indicate regions where air masses passed over a greater proportion of the time before arriving at the sampling site. The shaded area in these maps are analogous to air sheds for the sampling /receiving site.

Several models of regional and global scale POPs transport in the environment, including the atmosphere, exist (Chapter 4 of the RBA/PTS Global Report, UNEP, 2003). They simulate the large scale spatial and temporal distribution of a POP compound including the processes of direct emissions to the atmosphere, transport and dispersion on winds, chemical transformation in the atmosphere, and air-surface exchange. These models are either coarsely resolved box models (Breivik and Wania, 2002, MacLeod et al., 2001, Wania et al., 1999) or meteorology-based models with high spatial and temporal resolution (*e.g.* Koziol and Pudykiewicz, 2001, Semeena and Lammel, 2003, Hansen et al., 2004). In either case the size of the model domain ranges from regional to global. These models can be useful in network design and can be evaluated using POPs observations. The data together with the models may be used to support the evaluation of the effectiveness of measures taken to fulfill the Stockholm Convention. This will likely be an iterative process where differences between model predictions and measurements are identified and used to improve model design and measurement strategy. Because of their inherent complexity, it is envisioned that the direct use of transport models in the approach discussed above may be limited to groups/programmes with access to this expertise.

A simpler alternative for characterising transport to sites is the ‘Remoteness Index’, which integrates many of the concepts/techniques discussed above (Waldow et al., 2010). The remoteness index can be used for making informed decisions regarding the geographic location of sampling sites based on potential inputs from regional and global sources. It can also be used to interpret monitoring data spatially and temporally. The remoteness index approach uses emissions scenarios for various chemical classes and applies real meteorology in a global transport model framework to predict the geographic extent of impact. Remoteness index maps have been constructed based on emission scenarios for either industrial or agricultural chemicals. Global distributions of the remoteness index are shown in Fig. 4.1.3. Detailed, regional maps of the remoteness index can also be found in von Waldow et al. (2010).

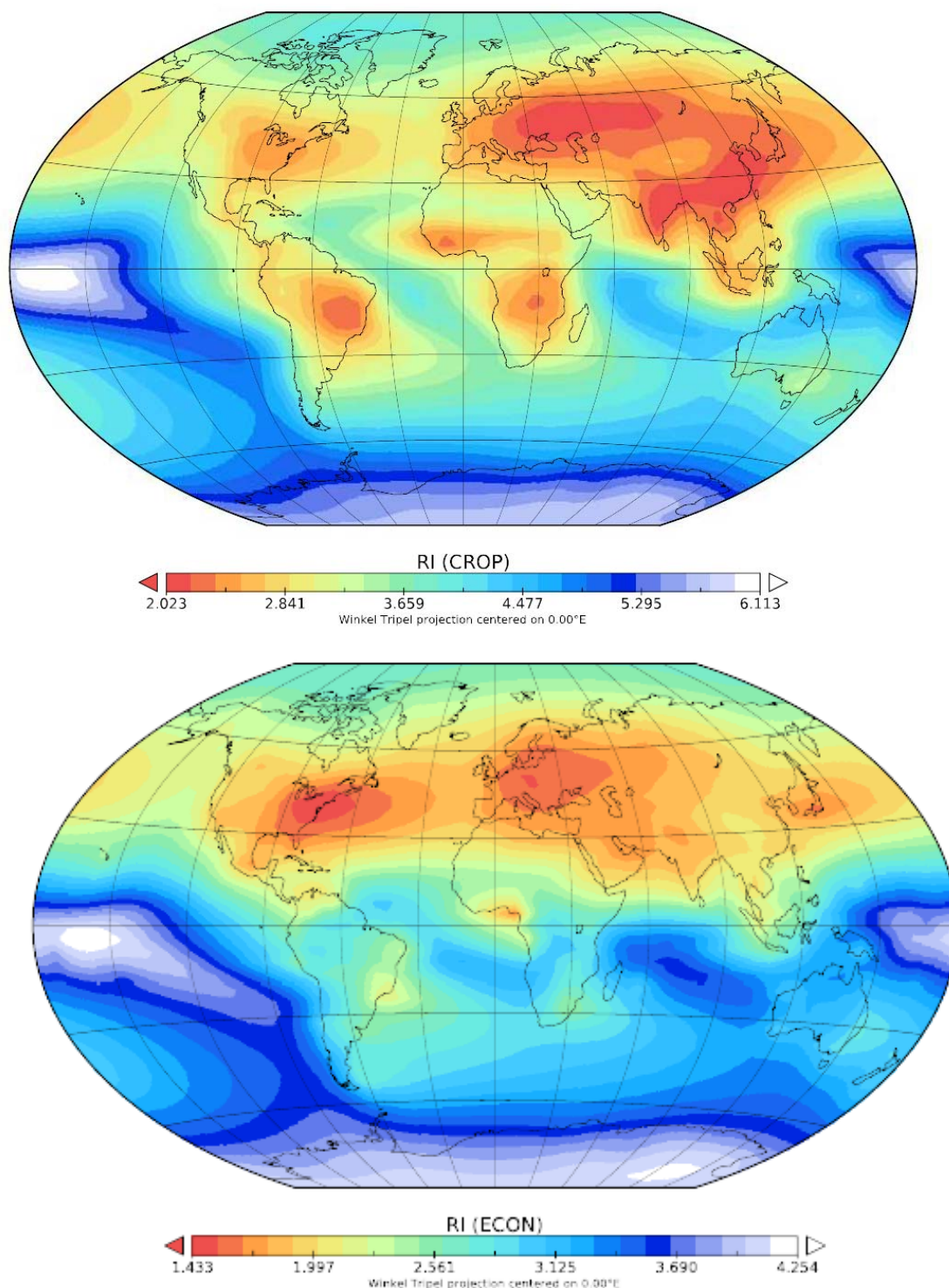


Figure 4.1.3: Global distribution of remoteness index for the CROP (top) and ECON (bottom) scenarios. CROP refers to pesticide emissions and ECON refers to technical emissions (Waldow et al., 2010).

A comprehensive review and evaluation of modeling approaches for quantifying the extent of long-range transport of POPs in the Northern Hemisphere was recently completed by the Task Force on Hemispheric Transport of Air Pollution (TF on HTAP) (UNECE, 2010). This is a working group of the Convention on Long-Range Transboundary Air Pollution under the United Nations Economic Commission for Europe (the UNECE LRTAP Convention). The task force found that modeling studies for the most studied POPs are in reasonable agreement with available measurements of concentrations in the atmosphere. In the many cases, modeled and observed concentrations of POPs in the atmosphere agree within a factor of three to four or better, however, in some cases the differences can be substantial indicating that there may be large uncertainties in emission inventories, in modeling approaches, or

both. Global-scale modeling of POPs indicates that inter-continental transport with westerly winds within the Northern Hemisphere, and transport from temperate regions to the Arctic is occurring. For example, models indicate that more than 50% of PCBs currently being deposited to the Great Lakes region of North America are attributable to distant emission sources.

Special Considerations for PFOS

Any air monitoring strategy investigating the occurrence and/or long range transport of PFOS to remote regions should include PFOS derivatives and precursor compounds. The gas-phase transport of PFOS is limited because it is an ionizable chemical (Table 4.1.1) that partitions strongly to water and in the atmosphere will partition to aerosols. The occurrence of PFOS at background and remote sites occurs through an atmospheric pathway that is mediated through the long-range transport of more volatile precursor chemicals that ultimately degrade to PFOS. Therefore in order to understand the occurrence of PFOS at background sites, it is necessary that these derivatives/precursors are monitored in air.

This strategy is consistent with COP4 Decision 4-17 that lists perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride to Annex A and B of the Convention. The decision refers to the draft risk management evaluation report of the Persistent Organic Pollutants Review Committee (POPRC) [UNEP/POPRC.2/17/Add.5, UNEP/POPRC.3/20/Add.5 and UNEP/POPRC.4/15/Add.6.] which for regulatory purposes adopts the European Union (EU) definition of PFOS. Under this definition PFOS includes all molecules having the following molecular formula: $C_8F_{17}SO_2Y$, where $Y = OH$, metal or other salt, halide, amide and other derivatives including polymers (European Union, 2006). Compounds targeted for air monitoring are listed in Chapter 2, Table 2.2.

Recently, Ahrens et al. (2011, 2012) have evaluated air sampling approaches for PFOS and precursor compounds and evaluated their particle-gas partitioning. These studies highlight the special considerations that are required when sampling these compounds in air using conventional high volume samplers or passive sampling approaches. Air sampling of PFOS and related chemicals is discussed further in the section below and in 4.1.3.

4.1.2 Sample matrices

Ambient air is an important matrix because it has a very short response time to changes in atmospheric emissions and is a relatively well-mixed environmental medium. It is also an entry point into food chains and a global transport medium. Air data are required to validate atmospheric POPs transport models. As discussed previously, some existing sampling networks (both active and passive) have contributed baseline data to the first global monitoring report and are summarized in Fig. 4.1.1.

POPs Associated with Particles in Air

Many POPs are semi-volatile chemicals that exist both freely dissolved in air and attached to particles. Their proportion on particles increases at lower temperatures due to a reduction in the chemical's volatility. The extent of partitioning onto particles will affect a chemical's fate and transport in the environment. Particle-associated chemicals are typically deposited closer to sources and are less subject to atmospheric transport. However, particle-association may also preserve some classes of POPs and protect them from atmospheric degradation reactions. Atmospheric fate of particle-associated chemicals is an area that requires further study.

When reporting air concentrations of POPs, it is important to distinguish gas-phase versus particle-phase results and/or indicate when the total of these two phases has been measured. Analysis of the particle-phase is particularly important for the PCDD/Fs and some of the newly listed POPs added to the Convention that partition appreciably to particles (e.g. PBDEs, PFOS). For instance, it has been noted that the polyfluorinated chemicals partition to particles differently compared to the conventional POPs and that new partitioning relationships will need to be developed for this compound class (Shoeib et al., 2005; Goss et al., 2006). Furthermore, studies have shown that substantial sampling artifacts may exist for PFOS and related chemicals due to sorption of gas-phase compounds to the glass-fiber filter that is used to assess the particle-phase component (Arp and Goss, 2008). Recent analysis by Ahrens et al. (2011, 2012) provides additional guidance for air sampling PFOS and related compounds in air. A new partitioning model for PFOS is described which takes into account the ionizability of PFOS (Ahrens et al., 2012).

Active air samplers typically include a pre-filter for capturing particles. This filter can then be extracted and analysed separately. However, the ability to accurately measure the particle-phase component is confounded by blow-off/on and sorption artifacts (Bidleman and Harner, 2000). Denuder samplers, in which the gas-phase is collected first, followed by the particle-phase, is an alternative method for overcoming these limitations and artifacts (Lane, 1999). However, denuders are currently not capable of the higher volume flow rates of conventional high volume samplers so longer sampling times are often required to detect trace levels of air contaminants.

The ability of passive samplers to capture particle-phase compounds is an area of ongoing study (Klanova et al., 2008; Tao et al., 2007). A 3-year evaluation of PUF disk against active samplers suggested that the particle-phase sampling of PUF disks samplers is reduced relative to the gas-phase rate (Klanova et al., 2008). However, more recent studies (Harner et al., in prep; Ahrens et al., in prep.) suggest that the PUF disk sampling chamber used under the GAPS Network does not discriminate between gas- and particle-phase compounds *i.e.* that a total air concentration is obtained with both phases collected at a similar sampling rate of $\sim 4 \text{ m}^3/\text{day}$. This is an area of ongoing study.

4.1.3 Sampling and sample handling

Air sampling requires the following capacities: (1) active and passive air samplers, (2) trained station personnel to operate and maintain the high-volume samplers, (3) meticulous preparation of clean sampling media in the laboratories performing the extraction procedures and chemical analysis. Sampling methods and QA/QC procedures should, as far as possible, be adopted from existing air monitoring programmes for POPs, but they will need to be adapted to and validated for the specific conditions, concentration levels and temperature at the sampling sites. High volume and passive sampling approaches are detailed below. Other sampling strategies are envisioned that may produce comparable data for national and regional reporting and these should also be considered. Although some indirect approaches such as sampling vegetation and deposition are valuable parameters for assessing environmental loadings, they should not be used to assess air concentrations quantitatively.

Efforts to avoid and minimize sample contamination are particularly relevant for some of the newly listed POPs. Many new POPs (*e.g.* PBDEs) exist in high concentrations in indoor environments, including laboratories where samples may be processed and stored. The newly listed POPs may also exist in commercial products and storage vessels that may contribute to the level of contamination. Special QA/QC considerations for newly listed POPs are outlined in section 4.1.4 and in Chapter 5.

High volume sampling

Networks that employ high volume air samplers to measure atmospheric POPs are summarized in Fig. 4.1.1. In almost all cases these networks employ sampling heads with size-selective inlets for collecting particles below some cut-off size threshold, typically particles smaller than 10 micrometers diameter. Sampling should take place using techniques practiced by routine long term monitoring networks in temperate areas (*e.g.* Fellin et al., 1996; Environment Canada, 1994) and sub-tropical to tropical regions (*e.g.* Ministry of the Environment of Japan and the National Institute for Environmental Studies). These groups recommend the technique of separating particles from gases using the combination of glass fibre filters in series with two gas absorbents. The nature of the type of absorbents used needs to be matched to the needs of the regional monitoring programme and target analytes. Several possibilities exist which are favoured for long term measurements and should be selected by experienced experts planning a regional study:

For the particle-phase,

- a glass or quartz fiber filter is typically employed. Teflon filters are not recommended due to contamination issues with PFOS and related compounds.

For the gas-phase,

- Two PUF plugs recognizing that some volatile chemicals (*e.g.* chlorobenzenes) will not be trapped efficiently. In this case, keep sample times short (*e.g.* especially when it is warm);
- PUF/XAD combination generally extracting and analyzing both media together;
- PUF followed by active carbon fiber felt disks.

Two absorbents are necessary to check periodically for breakthrough losses and to avoid substantive losses for some relatively volatile compounds (*e.g.* HCB), especially in tropical areas. The addition of higher-capacity sorbents such as XAD and active carbon as described above helps to improve capture efficiency of the more volatile and/or polar compounds. However, it should be noted that higher capacity sorbents may also lead to higher blanks and are more difficult to fully extract/ and clean. The need for low blanks should be balanced against the need for sorptive capacity of the sampling matrix.

The sampling schedule is also an important design consideration that will partly depend on available budget. Samples could be taken intermittently (*e.g.* approximately once every week or every 2 weeks) or continuously (weekly integrated) with care taken to minimise analyte breakthrough. Breakthrough can be minimized by using a higher capacity sorbent or a reduced air flow rate (sample volume). Breakthrough is also minimized at cold ambient air temperature when the sorptive capacity of the sampling matrix is increased. Field blanks should be taken every several samples. Field blanks are treated in the same manner as samples including placement in the sampler housing, except no air is drawn through them. In some cases air is drawn through the field blank but only for a very short period of time (*e.g.* seconds to minutes). The method detection limit (MDL) is often based on the levels of target analytes in blanks, rather than by the sensitivity of the analytical instrument (see section 4.1.4).

Absorbents are pre-treated prior to sampling as described in Fellin et al. (1996). Filters are sometimes also pre-treated by baking at high temperatures. Samples should be put into the sampling head using environment and handling practices that are free of contamination and volatilization losses. Many POPs are semi-volatile and may evaporate from sampling media if they are warmed appreciably above ambient temperatures. After sampling, samples and field blanks are extracted in the appropriate solvent (*e.g.* hexane and dichloromethane are common) by placing them in a Soxhlet extractor with 450 ml solvent are reduced in volume down to approximately 20 ml (*e.g.* see Fellin et al., 1996). Other extraction techniques such as accelerated solvent extraction, microwave extraction and sonication are also used, depending on the target compounds. These extracts are then split into two, placed in pre-weighed pre-cleaned vials, and sealed. One half is shipped to the laboratory and the other half archived. This archive is extremely important to recover from accidental sample loss during shipping and laboratory analysis. It also allows samples to be re-analyzed years later when analytical techniques may have improved and there is new information (such as on additional POPs) to be gained. Specimen banking is discussed further in Chapter 8.

Passive sampling

Networks that employ passive air samplers to measure atmospheric POPs are summarized in Fig. 4.1.1. Passive air sampling of POPs has undergone considerable technological development in the past decade. Early studies (Ockenden et al., 1998) and some continued efforts (*e.g.* UK-Norway transect study; Schuster et al., 2011) used/use semi-permeable membrane devices (SPMDs) to survey POPs over large spatial scales. Now, samplers made of polyurethane foam (PUF) disks (Shoeib and Harner, 2002) and XAD-based resin disks (Wania et al., 2003) have been developed and widely adopted (Figure 4.1.4). These samplers have been used to map the spatial variability of POPs in regional studies (*e.g.* Motelay-Massei et al., 2005; Gouin et al., 2005; Daly et al. 2007; Roots et al., 2010; Stafilov et al., 2011; Aliyeva et al., 2012; Adu-Kumi et al., 2012; Shunthirasingham et al., 2011; Meires et al., 2011) and on a continental scale in North America (Shen et al., 2004, 2005, 2006) and Europe (Jaward et al., 2004 a, b) and Africa (Klanova et al., 2008; Lammel et al., 2009). The first results from the Global Atmospheric Passive Sampling (GAPS) study have demonstrated the feasibility of these samplers for global spatial mapping at more than 60 sites around the world (Pozo et al., 2006; 2009; Shunthirasingham et al., 2010). The GAPS network has been complemented by the continental Monitoring Networks (MONET) in Europe and Africa (Klanova et al., 2009a, b) operated by Masaryk University, and monitoring efforts in Europe, East and West Asia coordinated through Lancaster University (Jaward et al., 2004a, 2004b, 2005). A key aspect of GAPS and MONET programs is technology transfer and capacity building – especially in regions lacking measurements of POPs in air. In 2010/2011, a UNEP-coordinated network of passive air samplers generated results in 31 countries in the Pacific Islands region, Africa and Latin America/Caribbean (UNEP, 2012, Bogdal et al., 2012).

For the passive sampler designs discussed above, the sorbing matrix is typically housed in protective chambers, which can either be shaped like a dome (Shoeib and Harner, 2002) or a cylinder (Wania et

al., 2003). Such shelters protect the sorbent from direct deposition of large particles, sunlight, and precipitation and help to diminish the wind speed effect on the sampling rate.

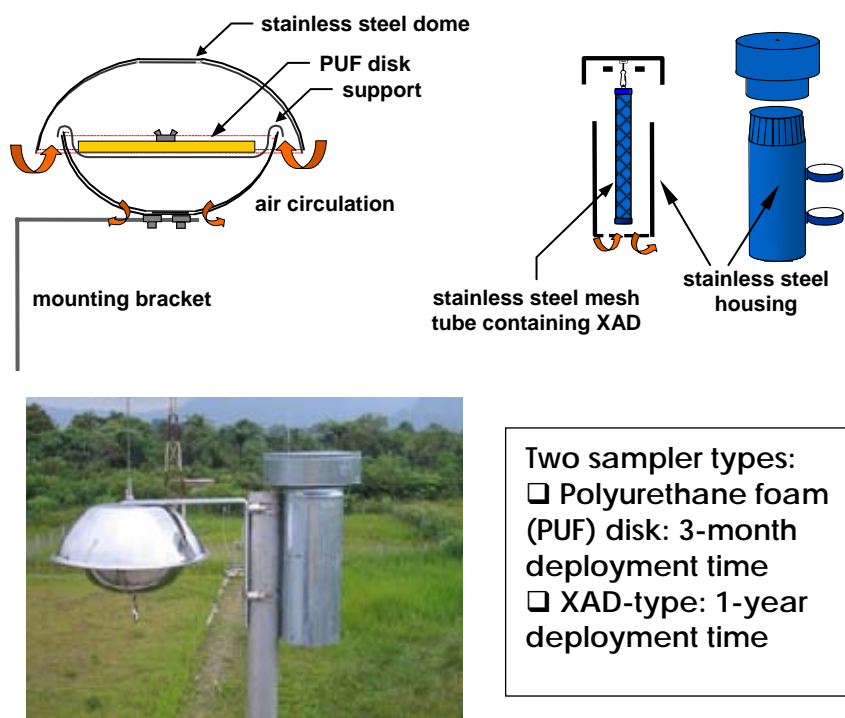


Figure 4.1.4: Schematics and photograph of PUF-disk (left) and XAD-based passive air samplers.

Sampling rates for PUF-disk samplers are typically in the order of $\sim 4 \text{ m}^3/\text{day}$ (Pozo et al., 2006, 2009) and so a 3-month deployment provides an equivalent sample air volume of approximately 360 m^3 , which is sufficient for the detection of most POPs. Shorter integration periods of 1 month have also been incorporated successfully. The wind-effect on sampling rate for the domed chamber design has been evaluated under controlled conditions (Tuduri et al., 2006), from field study results (Pozo et al., 2004; Klanova et al., 2006) and using flow simulation models (Thomas et al., 2006). Generally, the chamber is capable of dampening the wind-effect on sampling rate by maintaining the air flow within the chamber at less than $\sim 1 \text{ m/s}$. However, higher sampling rates have been observed at windy, coastal and mountain sites (Pozo et al., 2004, 2006, 2009).

A more precise measure of the air volume sampled may be achieved by spiking the sorbent prior to exposure with known quantities of “deuration compounds” or DCs. These are isotopically-labelled chemicals or native compounds that do not exist in the atmosphere and cover a wide range of volatility (assessed based on their vapour pressure and/or octanol-air partition coefficient, K_{oa}). The loss of deuration compounds over the sampling period is used to calculate the effective air sample volume (Pozo et al., 2004, 2006, 2009). The air concentration is then calculated based on this air volume and the amount of chemical collected over the sampling period. When deuration compounds are used it is possible to report semi-quantitative concentrations for PUF-disk sampler with an expected accuracy within about a factor of 2 (Gouin et al., 2005). This drawback of greater uncertainty in air concentration value associated with passive samplers is offset by the benefit that they are providing a time-weighted, average air concentration. For compounds that exhibit high temporal variability in air, a time-weighted sample may be more representative than a short-term sample (*e.g.* active sample) that may be biased by a high or low air concentration episode (Dreyer et al., 2010).

It is imperative to account for approach to equilibrium that may occur for the more volatile POPs (*e.g.* HCB) (Harner et al., 2004; Gouin et al., 2005; Pozo et al., 2006). This is mainly a consideration for PUF disk samplers that have lower capacities compared to XAD-based samplers. The effect is larger at warmer temperatures at which the equilibrium is shifted to the atmospheric gas phase, and the capacity of the sampling sorbents is greatly lowered. It is important to note that this limited capacity of the PUF disk is required to allow deuration compounds (of similar volatility to POPs) to be used to establish site-specific sampling rates.

In order to meet the challenges associated with air monitoring for more volatile and polar POPs, the sorptive capacity of PUF disk samplers was increased by impregnating with XAD powder (Shoeib et al., 2008). These new SIP (sorbent impregnated PUF) disk samplers (Fig.4.1.5) have been tested alongside conventional PUF disk samplers during a GAPS pilot study and were shown to produce comparable results for PCBs (Genualdi et al., 2010) and OCPs (Koblizkova et al., 2012). The SIP disk samplers were also able to capture the more volatile compounds of interest such as PFOS precursors (*e.g.* MeFOSE, EtFOSE, see Chapter 2, table 2.2), fluorotelomer alcohols (Genualdi et al., 2010), volatile methyl siloxanes (Genualdi et al., 2011) and penta- and hexachlorobenzene (Koblizkova et al., 2012). Field calibration of SIP disks has also demonstrated their potential application in longer time-integrated sampling of legacy POPs (*i.e.* longer than the conventional 3-month sampling used for PUF disks) (Schuster et al., 2012).

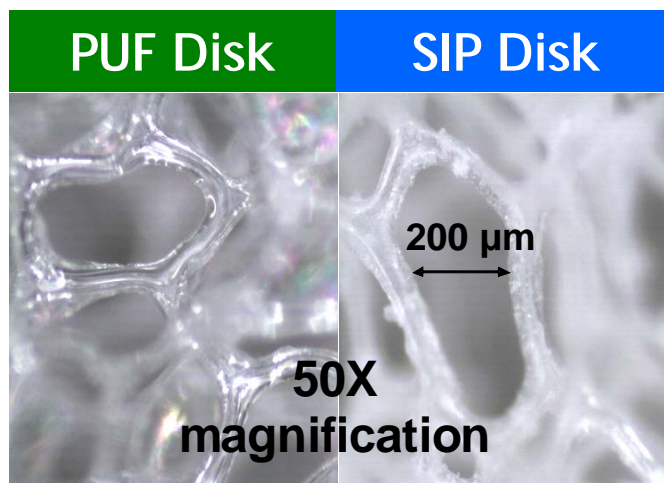


Figure: 4.1.5: Magnification of PUF disk and SIP disks showing porous structure of polyurethane foam and coating of ground XAD powder on SIP disks.

Sampling rates for XAD-based samplers are somewhat lower compared to PUF disks and SIP disks at $\sim 0.5 \text{ m}^3/\text{day}$ (Wania et al., 2003). These samplers are designed to integrate over an entire year with an equivalent sample air volume of approximately 180 m^3 . Wind tunnel experiments measuring the uptake rate over the wind speed range 5 to 15 m/s showed that the shelter employed in the XAD-based passive sampler dampens the movement of air close to the sorbent sufficiently, to assure that molecular diffusion is controlling the rate of uptake (Wania et al., 2003). Approach to equilibrium is not a concern for XAD-based samplers because of the relatively higher capacity of XAD (vs PUF) (Shen et al., 2002). Because of the high sorptive capacity of XAD samplers it is not possible to employ depuration compounds for assessing site-specific sampling rates.

In cases where larger air volumes are required over relatively short sample time periods but active sampling is not possible due to equipment limitations or electricity constraints, the flow through sampler (FTS) is a new type of sampler that may suit the purpose. The FTS aligns itself in the direction of the wind and collects analytes on a series of high porosity PUF disks, thereby sampling at much higher rates compared to conventional passive samplers (Xiao, et al., 2007). Air volumes for the FTS are determined through calibration against external or internal anemometers.

Prior to use, the sorbents such as the PUF disks and XAD-based resin, are pre-cleaned by sequential extraction (Soxhlet or accelerated solvent extraction) using a combination of polar and non-polar solvents (*e.g.* acetone: hexane and/or acetone followed by hexane; and toluene is typically used for dioxin analysis). Samples are stored in solvent-rinsed and gas-tight glass jars or metal or tetrafluorethylene containers prior to and after deployment. One field blank should be deployed at each site to assess potential contamination. These are typically inserted to the sampling chamber, removed immediately and then stored and treated as a sample. Samples are extracted using the same techniques as for active air samples described above. Similarly, analysis of extracts proceeds following procedures outlined in Chapter 5.

4.1.4 QA/QC and Data Treatment

A critical aspect for any air monitoring program is to implement and document a quality assurance and quality control (QA/QC) program. This is key to ensuring the credibility of the data and that it can be used to establish long-term trends and that it can be evaluated in terms of its comparability with results from other programs and sampling approaches (see discussion on comparability in the next section).

It is often the case that different monitoring programs employ different QA/QC protocols. It is important therefore that the treatment of the data is well documented in reports and publications so that when it is necessary, data sets can be harmonized and compared on the same basis.

An extensive review and assessment of quality assurance activities under the Integrated Atmospheric Deposition Network (IADN) is present in Wu et al. (2009). QA/QC and data treatment procedures that are used under the international AMAP air program are presented in Fellin et al., (1996). QA/QC protocols for several international air monitoring programs are included in Annex 5.

Interlaboratory exercises are often used to assess the effectiveness of QA/QC practices among several participating labs and to provide a measure of interlab comparability. This usually involves the circulation and analysis of a common standard or reference sample, often at two or more concentration levels. Recent international interlaboratory studies for POPs with a focus on air have been conducted through AMAP/EMEP/NCP (Schlabach et al., 2012), UNEP (2012, Abalos et al., 2012, van Leeuwen et al. 2013), and through an International Polar Year project, INCATPA (Su and Hung, 2011). Results from these studies are useful for evaluating interlaboratory variability for different POPs classes. The issue of data comparability is discussed further below.

QA/QC considerations

In addition to the references above that describe QA/QC procedure for international air monitoring programs, a few key aspects are described briefly below. Some of these challenges are particularly applicable to the newly listed POPs.

Blanks:

Method or lab blanks – This is usually done by using a clean matrix and/or solvent and treating as a sample, taking it through the entire methodology in order to assess contamination. It is useful to run method blanks prior to starting a campaign to ensure the integrity of the methodology. Method blanks are particularly important for some of the newly listed POPs (PBDEs, PFOS and related compounds) which may be elevated in the laboratory environment. If contamination is an issue, blank test could be performed on different stages of the methodology to determine and isolate the source of contamination. Method blanks should be run routinely during processing of real samples, at least one blank for every 10 samples (*i.e.* 10%).

Field blanks - These are sample media (*e.g.* PUF disk, GFF, etc.) that are installed in the sampler and removed right away and then stored and treated as samples. Field blanks account for additional sources of contamination that may arise due to sample handling, transport and storage. Care should also be paid to avoid other potential sources of contamination that may arise from the sampler itself or nearby sources. For instances flame retardants or other substances (*e.g.* chlorinated paraffins and its impurities (Takasuga et al., 2012) that are used in electrical equipment or construction materials (*e.g.* PCBs in sealants).

Sampling Efficiency / Sampling rates:

Breakthrough check – In the case of high volume samplers, a second sorption matrix is placed in series to the first to assess breakthrough of gas-phase analytes through first matrix (*e.g.* PUF plugs, PUF/XAD cartridges). Breakthrough is particularly important for more volatile compounds. Some of the newly listed POPs such as PeCBz, HCB, and α -HCH are known to exhibit substantial breakthrough on PUF due to their volatility. Volatility and breakthrough increase at warmer temperatures.

Adsorption artifact – In the case of high volume samplers, some gas-phase compounds may sorb to glass- or quartz fiber filters which are intended to capture particle-phase compounds. For analysis procedures that treat gas- and particle-phases separately, this will result in overestimation of particle-phase partitioning. This artifact can be assessed by using a second filter in series with the first and

analyzing the two filters separately. Ionic compounds such as PFOS have been shown to have a substantial adsorption artifact (Arp and Goss, 2008). Note that Teflon filters should be avoided when targeting PFOS and related chemicals.

Recoveries and use of surrogates:

Sampling recoveries – labelled surrogates are added to the sampling matrix prior to collection of a sample (e.g., added to PUF in the high vol sampler) assess losses due to sampling. This approach usually overestimates losses.

Analytical / Method recoveries – Recoveries can be performed two ways: i.) external recoveries are performed by spiking the extraction solvent or clean sampling matrix with a mixture of target compounds prior to extraction and then taking it through the methodology. Recoveries performed this way are used to validate the method but should not be used to correct individual samples. ii.) internally, labelled surrogates are added to the sampling matrix just prior to extraction to assess losses during the extraction and work-up methods. The use of labelled surrogates helps to account for analytical biases introduced by matrix effects. Matrix effects are known to be a challenge for PFOS and related chemicals, therefore the use of internal surrogates are highly recommended. Internal recoveries are acceptable for correcting sample results.

Ideally sampling and method recoveries should be between about 70-130%. Compounds with recoveries below 50% should be reported with caution. Low recoveries are typically a problem for volatile compounds (e.g. PeCBz and HCB) due to blow-down (evaporation) losses during the sample concentration step. These losses can be minimized by a gentle blow-down procedure and keeping the final sample volume at ~1mL or greater. The choice of extraction and keeper solvents will also impact blow-down losses.

Detection:

Method Detection Limit (MDL) and dealing data that falls below MDL - The method detection limit is usually defined as the mean blank + 3SD. If field blank values are available these are typically used and preferred. The MDL is analogous to an outlier test for blanks. Compounds that are detected above the MDL value can be considered real and very unlikely to be due to blank variability. In this sense, the MDL value is used to 'qualify' data. Data that falls above the MDL are considered true or real. Data that falls below the MDL are often reported as BDL, <LOD or <MDL.

Note: in cases where analytes are not detected in blanks, the MDL is based on the instrument detection limit (IDL) value presented below.

Instrument Detection Limit (IDL) and dealing with data that falls below the IDL – The instrument detection limit is determined from the amount of analyte that will produce a signal:noise or 3:1 on the analytical instrument. This can be estimated by extrapolation of the result for the lowest concentration standard. The IDL value is compound specific and will also vary from day to day according to instrument performance and sensitivity.

Limit of Quantification (LOQ) - The LOQ convention is rarely used in trace air analysis with the exception of analysis of dioxins and furans. LOQ is typically defined as 3 times IDL or 10 times the signal: noise. These two conventions result in similar numbers.

Data treatment - Qualifying data, blank and recovery correction:

As mentioned previously, raw data is qualified as real if it exceeds the MDL value. These data may then be subject to blank correction (by subtracting the mean blank value). Blank correction involves subtracting the mean blank value. Recovery corrections should only be applied to blank-corrected data when sample-specific internal surrogates have been used *i.e.* isotopically labeled surrogates of target analytes.

For reporting purposes and to facilitate data handling tools/approaches, the preferred approach is to present data in the following formats:

1. Qualified raw data and blank-corrected data (*i.e.* raw data that has exceeded the MDL and was then blank corrected). The mean blank values and MDLs for each analyte should be specified.

2. Recovery-corrected data should only be reported when internal surrogates were used for each sample. Otherwise, results should not be recovery-corrected and external recovery values should accompany the data for assessing the methodology (data quality).

Whatever approach is used to report the data (*i.e.* blank corrected or not blank corrected; recovery corrected or not), it is important that this is documented clearly so that data can be later manipulated as required.

Regarding raw data that falls below the MDL (*i.e.* does not ‘qualify’) but is above the mean blank value; we suggest to report these data but to flag them in some way to indicate that the values have greater uncertainty.

Comparability

The issue of data comparability applies in several ways.

- i.) intra (within)-programme data comparability for the purpose of comparing air concentrations in time – *i.e.* deriving temporal trends
- ii.) inter (between- or among)-programme data comparability for the purpose of comparing air concentrations spatially and for modeling purposes.
- iii.) comparing data derived using different approaches or strategies *e.g.* active versus passive sampling

The derivation of temporal trends of POPs in air is critical for assessing effectiveness of control measures on POPs. This requires that a data set for a given program is internally consistent. Internal consistency can be achieved by adapting strict sampling protocols and laboratory QA/QC practices as discussed above to ensure that data are not influenced by factors other than real changes in air concentrations. Some of the long-term monitoring programs are often required to continue to use original analytical techniques that may be currently ‘out-of-date’, in order to ensure that contemporary data are consistent with samples analyzed ten or even twenty years ago. Any significant changes to the methodology should be accompanied by an intercomparison strategy to assess and quantify and correct for divergence.

Although less critical for effectiveness evaluation, inter-program comparability is useful for investigations of regional and global transport of POPs and in the context of model application and evaluation. Inter-program comparability can be assessed through intercalibration exercises. However, until recently only limited attempts have been made to do this for POPs in air samples. Su and Hung (2010) have recently completed a comprehensive and international intercalibration exercise for a wide range of POPs that included 21 participating laboratories from 7 countries. Their findings indicate that in general, interlaboratory differences of up to a factor of 2 can be expected but that intralaboratory precision was generally good with relative standard deviations typically <10%. At the time of writing this document (November 2012) similar intercalibration exercises for air were being undertaken and reported under a joint NCP/EMEP/AMAP exercise and the second Biennial Global Interlaboratory Assessment on POPs by UNEP that will include an air extract for the analysis of all 22 POPs (Schlabach et al., 2012; UNEP, 2012b).

A future goal to address inter-program comparability is to set-up master stations that include overlap between two or more sampling programs. In this way, sources of variability beyond just laboratory variability can be assessed. Some overlap of monitoring network sites is already occurring and could be exploited to evaluate this issue.

Data comparability in a broader sense also comes into play when reporting data from different sampling approaches (*e.g.* passive vs active; gas-phase, particle-phase or total concentrations) and strategies (*e.g.* time-integrated sampling or intermittent sampling such as 1 day in 10). A one-year field intercalibration study by Dreyer et al. (2010) demonstrated good comparability between high volume and SIP disk samplers for the polyfluorinated compounds (Dreyer et al. 2010). Even longer term comparisons of PUF disks and high volume air samplers have been established for several POPs classes at the Kosetice site in the Czech Republic. Figure 4.1.6 shows good temporal and seasonal comparability between the co-located active and passive air samplers.

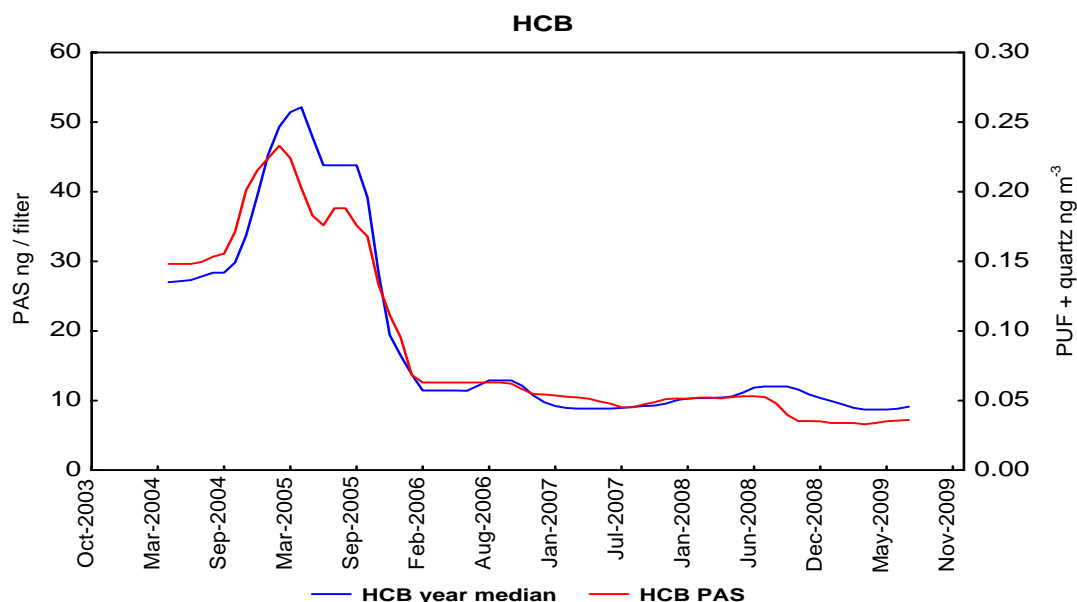


Figure 4.1.6: Comparison of long-term active and passive (PUF disk) air monitoring data for hexachlorobenzene (HCB) from Kosetice, Czech Republic.

It is also important to realize that observed air concentrations should be referenced to a specific site category as discussed earlier (section 4.1.1), rather than the country/state where the sample was collected. Air concentrations of POPs can vary by orders of magnitude within even relatively small countries so it is inappropriate to suggest that an air concentration result from only 1 or 2 sites is somehow representative of the entire country.

To summarize, a large amount of supplementary information is required for interpreting and comparing data, especially between programs. Efforts to handle and summarize these data would be greatly facilitated if the primary data were reported according to the guidance provided in this document. In most cases, air concentrations should be reported in units of concentrations (typically pg/m³) and include details on how the sample was collected, what the sample represents (gas- vs particle phase) and a description of the location (site category) (see section 4.1.1). In some cases it may be necessary to normalize sample concentrations to standard temperature and pressure to correct for variability in sample air volumes due to pressure and temperature extremes *e.g.* for high altitude or extremely cold sites, in cases where the samplers are not designed and calibrated to adjust automatically (Fellin *et al.*, 1996). Some passive sampling studies have reported results in units of mass per sample due to uncertainty in the effective air sample volume. In this case it is important that the data be normalized to the duration of the sample (*i.e.* on a per day, per month or per year basis as appropriate) to improve comparability of reported data.

Reporting of un-aggregated vs aggregated data

For purposes of data handling under the GMP data handling tool, it is recommended to submit data in units of concentration in air, according to the frequency of sampling (*e.g.* weekly, monthly, seasonally-every 3 months, annually). These data can then be aggregated as required (*e.g.* annually) for future reporting. For instance, aggregation of data sets may be required to perform comparable time series analysis to investigate changes in concentration with time.

If reporting of un-aggregated data is not possible, then at a minimum, data should be reported that is aggregated as the yearly mean (arithmetic mean) air concentrations for given sampling sites, in units of pg/m³. The issue of handling aggregated data is discussed further in Chapter 3.

4.1.5 Considerations for time trend analysis

Chapter 3 (Statistical Considerations) outlines key considerations for conducting trend analysis on environmental data including a section dealing specifically with air data. Sampling frequency and site

selection (including sources of emissions and transport to the sites as discussed in section 4.1.1) also factor into the statistical treatment of data. This integration of measurements with models and emissions information is further elaborated in section 4.1.7.

As demonstrated by high resolution data sets from some long-term monitoring programs, trend analysis for high volume (active sampling) air data, has additional complexity. This is due to the responsive nature of air (air has a relatively low capacity for POPs) coupled with relatively short sampling durations for high volume air samples (typically days). Consequently, time series data for air typically demonstrate periodicity that may occur seasonally or over shorter time intervals (Venier and Hites, 2010). Further, these 'harmonics' are compound- and site- specific. Digital Filtration (DF) (Hung et al., 2002) and Dynamic Harmonic Regression (DHR) (Becker et al., 2006) are two techniques that have been used successfully to assess time trends. Different interpretations of temporal trend data are possible depending on the time series model that is used (Venier et al., 2012).

Figure 4.1.7 shows long-term air monitoring data for HCB from the Zeppelin Mountain site operated under the AMAP program (Hung et al., 2010). The long term trends and seasonal cycles are evident. The increase in HCB concentrations since 2003 is intriguing and may be due to increased and continuous use of pesticides containing HCB. It is also speculated that this increase is due to climate-effects that results in reduced ice cover in the region resulting in increased volatilization of previously deposited chemical.

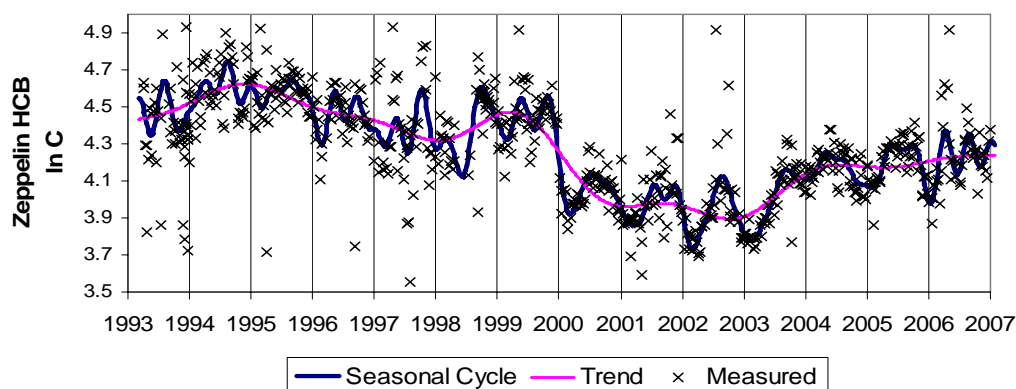


Figure 4.1.7: Temporal trend of hexachlorobenzene (HCB) in air at Zeppelin Mountain site, 1993-2007.

In the case of new air monitoring programs for POPs, including passive sampling data, the issues discussed above may be less relevant, especially if the data are collected with reduced frequency or using time-integrated passive samplers. In these cases, primary data (as outlined in section 4.1.4) should be reported to the GMP to provide a common basis for data handling.

4.1.6 Climate Effects

The topic of climate change and its impact on contaminant pathways introduces even more complexity for temporal trend data analysis (Macdonald et al., 2005; Ma et al., 2011). Correlations between air concentrations of POPs and low-frequency climate variations (*e.g.* North Atlantic Oscillation - NAO, El Niño-Southern Oscillation (ENSO) and the Pacific North American (PNA) pattern) have already been demonstrated (Ma et al., 2004). This is of special concern in regions such as the Arctic where expected temperature increases and associated geophysical cycles are maximized (Macdonald et al., 2005). In addition to temperature increases, other meteorological disruptions associated with climate change (*e.g.* increased floods, droughts) may affect POPs mobility and air concentrations trends.

All of these topics should be considered when interpreting trends. Because of the site specific nature of these processes it is important that trends be considered on a site-by-site basis rather than implying regional coverage with the given number of sites. This strategy will also help to ensure comparability of data.

The issue of climate change on POPs was recently addressed by an AMAP/UNEP expert group to address the mandate given to the Global Coordination Group (at COP4) to assess climate influences on the levels of POPs measured in the environment and in humans and how these influences may interfere

with present and future evaluations of the effectiveness of the Stockholm Convention measures (UNEP, 2011)..

Key messages of the report that relate to climate influences on POPS in air include:

- Climate change may affect primary emissions to air of POPs by changing their rate of mobilization from materials or stockpiles, or by altering use patterns. The effect of temperature on primary emissions of semi-volatile POPs is probably the most important effect and stronger than many other effects of climate change on the environmental cycling of POPs. This increase in primary emissions will counter efforts of the Stockholm Convention to reduce emissions of POPs. Higher temperatures will also increase secondary emissions of POPs to air by shifting the equilibrium partitioning between air and soil, and air and water. Releases from environmental reservoirs such as soil, water and ice will also increase due to these higher temperatures. The expected increase in the incidence of vector-borne disease, such as malaria, associated with climate change may lead to enhanced demand for and release of DDT in some regions.
- There are several main factors related directly to climate change which will influence the environmental fate of POPs, including their long-range transport: (i) the strength of secondary re-volatilization sources; (ii) wind fields and wind speed; (iii) precipitation rates; (iv) ocean currents; (v) melting of polar ice caps and mountain glaciers; (vi) higher frequency of extreme events; (vii) degradation and transformation; (viii) partitioning; and, (ix) biotic transport.

4.1.7 Integration

The interpretation of air monitoring data for POPs to satisfy questions on effectiveness of control measures or questions dealing with regional and global transport of POPs is complex and involves many interacting and competing issues. Observed temporal trends may be due to regulation efforts but as the previous sections have shown, they can be due to other factors such as climate effects. Furthermore, some chemicals are subject to time lags as long as several years from the time they are regulated to the time when a resulting decline in environmental concentrations due to their persistence (Gouin et al., 2010).

Informed decisions regarding the fate and behaviour of POPs requires an integration of information on chemical properties, emissions, models results and monitoring data (Fig. 4.1.8). This integrated approach is also an iterative process in which one type of information may inform the other and lead to re-evaluation. For instance, spatially resolved monitoring data may allow the application of new types of models. Discrepancies between model results and measurements may lead to a review of estimated emission scenarios.

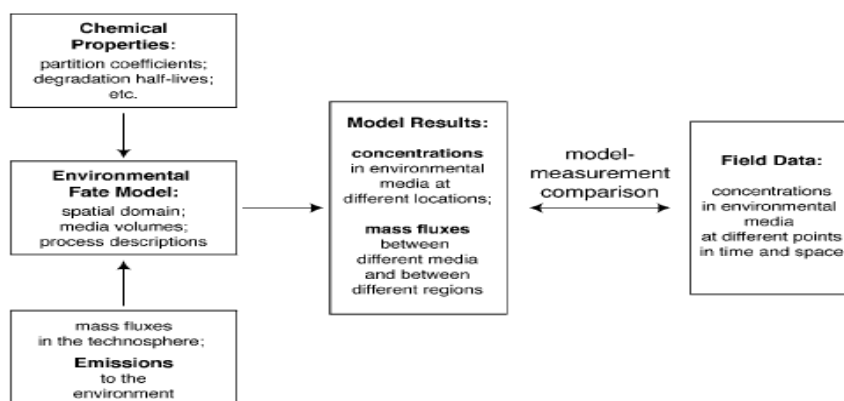


Figure 4.1.8: Integrated information required to make informed decisions on the environmental fate of a chemical. (Scheringer, 2009)

4.1.8 References

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EMEP	http://www.emep.int.html

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Lancaster Environment Centre	http://www.lec.lancs.ac.uk/
MONET / RECETOX / GENASIS database	http://www.recetox.muni.cz ; http://www.genasis.cz
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4.2 Human milk and maternal blood as biological indicators

4.2.1 Introduction

The objective of human monitoring within the GMP is to identify temporal and, as appropriate, spatial trends in levels of POPs in humans. The programme also assists regional capacity building in developing countries by supporting technical/analytical capability to detect regional trends of POPs in humans.

Human milk and human maternal blood have been used as markers of exposure of humans to a number of POPs for several decades. Both these sample media show comparable temporal trends in a particular population because they integrate environmental exposure as well as dietary exposure related to different consumption habits. Furthermore, they provide relevant information on POPs transfer to infants and potential health effects.

The main purpose of these programs was to assess the body burden of contaminants in newborns. In addition, they reflect integrated contamination at a high trophic level, the magnitude of this contamination and different dietary habits. Furthermore, such studies are also used as general biological monitoring tools. Thus, human milk and human maternal blood monitoring programs have been designed to assess levels of environmental pollution by hazardous substances in different areas within and across country borders. Trends in exposure levels and effectiveness of regulations have been evaluated by comparing these assessments with earlier investigations.

Human milk

Organized human milk monitoring programmes have been implemented by WHO. A few countries have systematic human milk monitoring programmes that have tested considerable numbers of women over time using consistent sampling methods. WHO organised five rounds of exposure studies in 1987-1988, 1992-1993, 2000-2001, 2005-2007 and 2008-2010 on levels of specific POPs in human milk (WHO 1989, 1996, van Leeuwen and Malisch 2002, Malisch and van Leeuwen 2003, Malisch et al. 2010).

The main objectives of these studies were: 1) to produce more reliable and comparable data on concentrations of PCBs, PCDDs and PCDFs in human milk for further improvement of health risk assessment in infants, 2) to provide an overview of exposure levels in various countries and geographical areas, 3) to determine trends in exposure levels.

Nineteen European countries, as well as other countries around the world, participated in the second round, in which concentrations of PCBs, PCDDs/PCDFs were determined in milk samples collected in a total of 47 areas. The third round of the WHO-coordinated exposure study was initiated in 2000. In order to collect data in more countries, also beyond the European region, the study was organised in collaboration with the International Programme on Chemical Safety (IPCS) and WHO Global Environmental Monitoring System/Food Contamination Monitoring and Assessment (GEMS/Food). In this study, 18 countries participated and milk samples from 62 different areas were analysed. For some countries, a pilot study of concentrations of other POPs than PCBs and PCDDs/PCDFs was also included, for which pooled human milk samples were used. The fourth round of exposure studies was organised by WHO GEMS/Food in 2005, including all twelve POPs. The fifth round was jointly organised by WHO and UNEP in 24 countries around the world. Results are available and indicate that this kind of survey is practical, feasible and sustainable.

Human blood

The Arctic Monitoring and Assessment Programme (AMAP) organized comprehensive human maternal blood plasma⁹ monitoring with standardized protocols for specimen collection and analysis in the Arctic since the early 1990s. Maternal blood plasma, supplemented with some human milk data have been used in assessing PCBs, organochlorine pesticides and human health (AMAP 1998, 2004). In the last assessment, PBDEs and perfluorinated compounds were also included in the monitoring data (AMAP, 2009).

⁹ Immediately after taking a sample of the maternal blood the blood plasma is separated and stored / pooled for analysis

Through this programme, an international QA/QC program for blood plasma analysis has been developed, with systematic ring tests of reference materials and unknown plasma shipped to all participating laboratories three times a year, allowing for new laboratories to produce reliable data on human maternal plasma as well as cord blood (CTQ, Quebec, Canada). All laboratories producing data for the AMAP assessment reports have to prove their performance in this international intercalibration study. Data from the AMAP reports as well as the QA/QC performance of the AMAP reporting laboratories show that blood survey is practical, feasible and sustainable.

Several AMAP partners are assisting to develop the laboratory capacity in Eastern Europe, as well as in many developing countries, such as Vietnam, South Africa and Brazil. There is a continuing need for education of personnel, as well as implementation of new technology. This is an opportunity to increase the amount of available and comparable international data by expansion of existing international QA/QC programmes to those new laboratories willing to join an educational programme for their staff and regular ring tests. The North American Commission for Environmental Cooperation (CEC) is undertaking a tri-national maternal blood monitoring program in Mexico, Canada and the USA. The CEC program utilizes the approach and protocols developed by AMAP. A significant component of the CEC programme is to build laboratory capacity for human environmental monitoring in Mexico. This involved laboratory training of Mexican technicians in Canada, sharing of known and unknown reference materials and participation in the AMAP QA/QC ring test.

All Arctic countries have participated in the first rounds of AMAP assessments and the majority of the countries have data from different geographical areas within each country, allowing for a better identification of sources of exposure etc. In addition to the Arctic countries, data from several southern developing countries have also been assessed for comparative purposes. In the last round considerable amount of new data on human levels of PFCs was presented, allowing for a good Arctic overview on human PFC levels. Considering that the majority of other international studies have been in blood, comparisons to other parts of the world have been feasible.

Some general methodological considerations with regard to the choice of sample medium

There are three main tissues where the POP levels are normally measured in order to assess the exposure to the child: maternal blood, cord blood and mothers milk. Several studies have shown correlation between the levels of contaminants in these compartments (Jarrell et al. 2005, Muckle *et al.* 2001). Studies of the relationship between breast milk, maternal blood and cord blood levels of POPs have been carried out. A summary of some general conclusions are listed below:

Levels of POPs in maternal blood correlate well with the levels in human milk, on a lipid weight basis (Anda et al. 2007). Thus milk and maternal blood can be used for biomonitoring and monitoring of POPs on an equal basis.

Maternal blood contaminants provide the exposure index for foetal circulation; maternal blood contaminant levels are most likely also the general driving force for human milk concentrations of POPs, and thus also of the exposure of the baby. Mothers' milk is one of the most sensitive exposure medium for the baby in terms of postnatal development.

A number of countries have established long term monitoring programmes that follow a sampling strategy that measures exposure to POPs across the general population. These valuable studies will be welcomed contributions to the Global Monitoring Plan.

The analytical procedures are becoming more sensitive and less expensive, for both blood and breast milk.

Overall comments with regard to choice of sampling medium, study group and number of samples

Human milk and human blood are both appropriate sample media for assessing POPs exposure in humans. Furthermore, both these media can be used to demonstrate possible temporal trends and regional variations in levels, and thus show effectiveness of regulations of the use of POPs. For PFOS however the levels are much higher in blood and this is the preferred matrix

- Human milk sampling is non-invasive and milk can generally be obtained from lactating mothers in reasonable quantities. In certain populations it may however be difficult to obtain human milk samples.
- Blood sampling is invasive, but does not exclude any gender or age groups, and sampling of mothers prior to giving birth may readily be achieved. However, blood sampling may not be acceptable in certain cultures.
- Biological samples of human origin, like blood and milk, should always be considered a potential biohazard. Necessary precaution procedures should be applied to both sampling and handling of all samples, not only in situations where one may expect a problem, *e.g.* HIV-positive serology and hepatitis.
- The limit of detection for POPs will in general be lower in milk than in blood. The reason for this is partly the difference in lipids between the media and the fact that larger volumes of milk as compared to blood can normally be obtained.
- For PFOS the limit of detection will be considerably lower in blood than in milk as only a small (1%) and variable percentage is found in milk. When the limit of detection is approached the analytical precision will decrease.
- An important consideration in the choice of human milk and maternal blood as biological indicators and the fact that through breast milk we will only obtain information from a specific part of the population both with regard to gender and age. Blood sampling can be designed to explore alternative representative groups in a population, *e.g.* men (specified age groups), youth groups of both gender, school children or infants, as discussed in the preceding section.
- A population study must be based on sampling and analyses of individual samples; human milk or human blood. Pooled samples might be considered for certain contaminants, such as the dioxins which are expensive to analyze and need larger sample volumes. A disadvantage with pooling is that information on individual variation is missed.
- In order to reduce sample variance and facilitate comparability a stratified sample design should be adopted. This should be based on demographic information collected in specific questionnaires, *i.e.* age, residence, occupational history, smoking habits, current and previous diet etc.
- Selection of study groups should be based on known exposure patterns, global or local. The groups with known high exposure levels are more sensitive to changes in the environment and will provide better indications in trend analyses. Even in countries with very limited background information one might be able to select population groups of interest, such as rural versus urban; fish eating populations versus rural agricultural populations with high exposures to pesticides; populations living in areas with re-introduction of DDT for malaria prophylaxis etc.
- The choice of milk or blood depends very much on the practical implementation regionally or locally, as well as on the compounds to be analyzed. Two examples:
 - In the Arctic many indigenous women deliver their babies and go home to the tundra before they have started their milk production. To collect colostrum provides a very different medium than the fully developed breast milk 2-3 weeks after delivery. It is not possible to trace the women at the right time for breast milk collection. A blood sample will solve that problem.
 - In certain areas sampling of maternal blood might be problematic. In those cases breast milk is the best matrix. Comparable information from both media can then be obtained.
- Trained personnel are crucial at the sampling and analytical stages. Standardized protocols, equipment and education of field personnel as well as laboratory personnel must be implemented.

The number of samples is crucial for the statistical power of a study. Power calculations must be applied carefully (see Chapter 3 on Statistical Considerations). Based on known sources of contaminants, both long-range transport and local sources, one should apply population stratification criteria for sampling as a way to achieve better comparability and reduce variability. To stratify a population consideration should be given to more critically exposed populations (not

occupational exposure) that could be the subject of a more detailed study including rural, urban and or populations subject to other types of exposure. Indigenous populations of the Arctic and in Africa have been shown to have different contaminant problems.

- Study sample size will depend on the circumstances, and to estimate the number of samples needed a number of factors have to be considered to achieve representative samples (see Chapter 3 on Statistical Considerations). The WHO has developed criteria for sample numbers depending on population size (ref WHO). However, new technologies and new, certified laboratories will provide the opportunity to begin epidemiological studies with individual results on a larger scale.

Assessing temporal trends of POPs in humans is important and this can be achieved in several ways. Figure 4.1.1 provides an example of individual breast milk samples, and figure 4.1.2 provide an example of using archived pooled blood samples. Both provide valuable information on changes with time in human POP concentrations. Common for both figures are the large number of sampling points over the time period studied, enabling detection of smaller variations and more certainty of the direction of the trend. For figure 4.2.1 statistical evaluation of the data indicated a small but significant decline in the levels of BDE 47 and BDE 99 from 1996 to 2006, whereas there was a significant increase in the concentrations of BDE 153 in the same period. The time span is however relatively short adding uncertainty to the trend. In Figure 4.2.2, the levels of PFOS and PFOA decreased significantly since approximately 2001. For PFNA and PFDA there was a continuous increase over the same period. Having a time trend consisting of only two time points can also contribute valuable information regarding changes between those two years (Figure 4.2.3). However, it is impossible to estimate the rate of change between the two time points and make predictions for the years following the last time point. In the case of PFOS the maximum concentration most likely occurred between the two time points and not before the first time point making it impossible to conclude about the current trend.

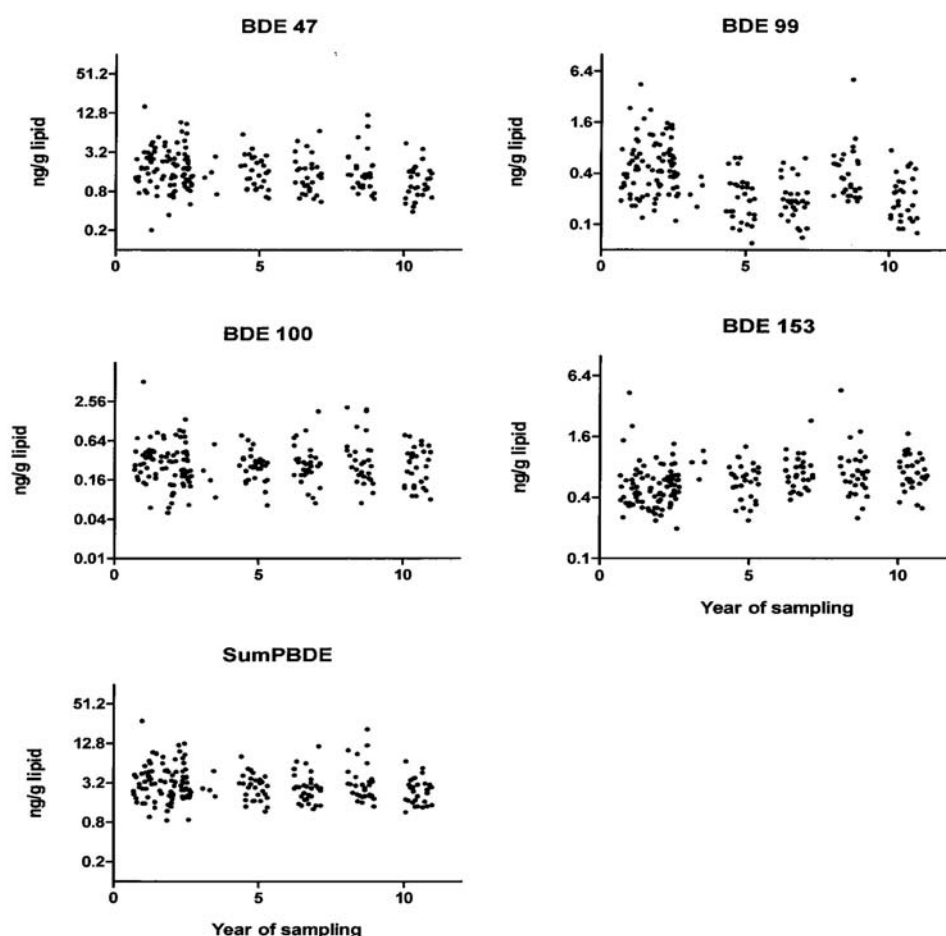


Figure 4.2.1: Time trends of PBDEs in individual breast milk samples. (Lignell et al 2008)

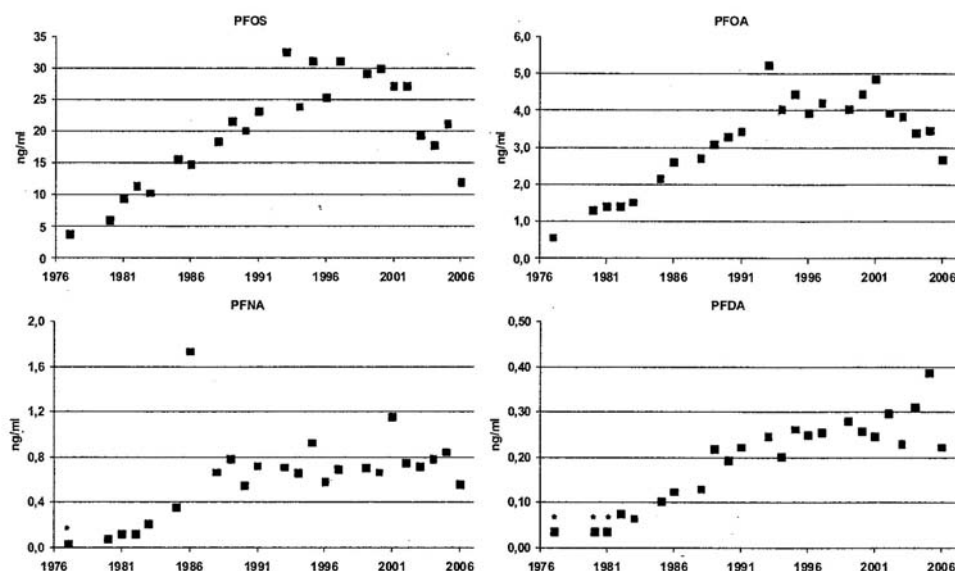


Figure 4.2.2: Time trends of PBDEs in individual breast milk samples and PFCs in pooled serum samples. (Haug et al. 2009)

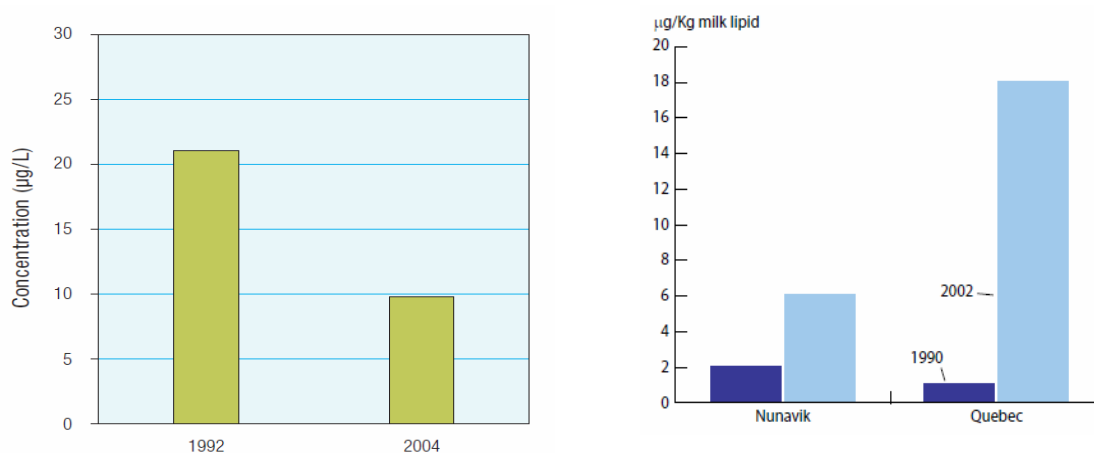


Figure 4.2.3: Two point time trends for PFOS in maternal plasma and PBDEs in breast milk samples. (Pereg et al 2003, Pereg et al 2007-2008.)

4.2.2 Analytical considerations for the newly listed POPs

There are some special considerations that need to be taken when analysing some of the newly listed POPs. These issues are addressed below for the compounds or compounds groups individually.

Chlordecone

The analytical determination of chlordecone is similar to the method for traditional POPs, but it binds stronger to silica/florisil columns and care must be taken not to lose it during clean up.

Hexabromobiphenyl

The analytical determination of hexabromobiphenyl is the same as for the determination of the traditional POPs. Particular attention needs to be given to the co-elution of PBDE 154 with PBB153 on a 30 m DB 5 column.

Lindane (γ -hexachlorocyclohexane)

This compound also follows the analytical methodology of the traditional POPs. The volatility of this compound requires some precautions during evaporation of solvents.

Alpha hexachlorocyclohexane and beta hexachlorocyclohexane

These compounds also follow the analytical methodology of the traditional POPs. The volatility of these compounds requires some precautions during evaporation of solvents.

Tetrabromobiphenyl ether and pentabromodiphenyl ether

The analytical determination of these groups of compounds is the same as for the determination of the traditional POPs.

Hexabromodiphenyl ether and heptabromodiphenyl ether

The analytical determination is the same as for the determination of the traditional POPs.

Pentachlorobenzene (PeCB)

This compound also follows the analytical methodology of the traditional POPs. The volatility of this compound requires some precautions during evaporation of solvents.

Perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOS-F)

Among the nine newly listed POPs listed under the Convention in 2009, perfluorooctane sulfonic acid (PFOS) and its salts do not follow the “classical” pattern of partitioning into fatty tissues, but instead bind preferentially to proteins in the plasma, such as albumin and gamma-lipoproteins, and in the liver, such as liver fatty acid binding protein (ref). This makes blood and liver the prioritised medium for PFOS. The general analytical issues when determining PFOS is discussed in the analytical section (see Chapter 5).

In contrast to the other POPs analysis of the ‘new’ fluorinated POPs including PFOS has only taken place since the beginning of 2000 when the first publications of PFOS in humans and the environment were published (Hansen et al., 2001, Giesy and Kannan 2001). The problems with the analysis and comparability of data were large and highlighted at a workshop in Hamburg and a subsequent paper (Martin et al. 2004). Several problems were highlighted including the purity of standard solutions, the quantification of standards branched and linear isomer, risk of laboratory contamination, no method validation available, the lack of (certified) reference material, standard solutions and labeled internal standards. To address several of these issues an international QA/QA study organized including human blood and plasma. The result of this study confirmed ‘the struggle for quality in the determination of PFCs in human and environmental samples’ (van Leeuwen et al. 2006) were a variation in the reported data of more than 30% was seen (RSD 32% and 56% for plasma and blood respectively) between invited expert laboratories. However strong improvements have been seen in subsequent years with better extraction and clean up techniques and the introduction of ¹³C labeled internal standards achieving RSDs of only 12-16% between more than 20 expert laboratories (van Leeuwen 2009, Lindström 2009). Some problem areas were solved including the quantification reporting on anion basis and include the branched PFOS isomers to report the total PFOS in ng/ml.

Due to higher albumin content, blood is considered the preferable and recommended medium to determine fluorinated compounds, but analyzing PFOS in milk samples is also a viable option with today’s technology. However there is limited breast milk data available. A strong association between blood and milk concentrations of PFOS have been reported (Kärman et al., 2007).

The levels in human milk are generally much lower 20-100 when reporting in ng/ml (Kärman et al. 2007, 2009, Tao et al. 2008, von Ehrenstein, Calafat et al. 2009, Sundström 2010) indicating that human milk is not a primary target for PFOS. This makes the analysis more challenging and is reflected in the results of a fourth QA/QC study on PFCs including PFOS on human milk, the variation between 20 expert laboratories was more than 35% (38% and 49%) for two pools of milk.

Kärman and Davies (2013) collected milk and serum samples from *primipara* women in Uppsala, Sweden in 2004, 2007, 2009, and 2011. 48 serum samples and 48 milk samples were collected and analyzed on a MS/MS system run in electrospray ionization mode. Levels of PFOS (linear isomer) were determined using in-house validated methods and quality control protocols. Excellent recoveries, reproducibility and accuracy were demonstrated: quality control samples were included in each batch to assess reproducibility and accuracy; further quality control was the successful participation in the 2009/2010 interlaboratory studies on milk (Kärman and Lindström 2013) and serum (Lindström et al. 2009).

PFOS (linear isomer) was quantified in all samples and concentrations ranged from 1.3 to 20 ng/mL in serum and 0.028 to 0.354 ng/mL in milk. The limit of detection was 0.05 ng/mL for serum and 0.012 ng/mL for milk. The concentrations found are in the range of other reported studies on PFOS in serum and milk.

Serum levels of PFOS were compared with levels of PFOS in human milk from the same mother. The regression analysis (Figure 4.2.4) showed that levels of PFOS measured in milk and serum were highly correlated, with a Pearson's correlation coefficient of 0.9171. Milk levels in this study are on average 1.55% of the corresponding serum levels. This value is in agreement with previous studies on similar serum to milk relationships, that have reported 1.09% (Kim et al. 2011), 1% (Kärman et al. 2007), and 1.4% (Thomsen et al. 2010).

Further, the study has also demonstrated excellent recoveries, reproducibility and accuracy. Two quality control (QC) milk and serum samples were analyzed with the other samples. Recoveries (average and range) of PFOS in the milk and serum samples were of 78% (51-90%) and 101% (81-110%), respectively.

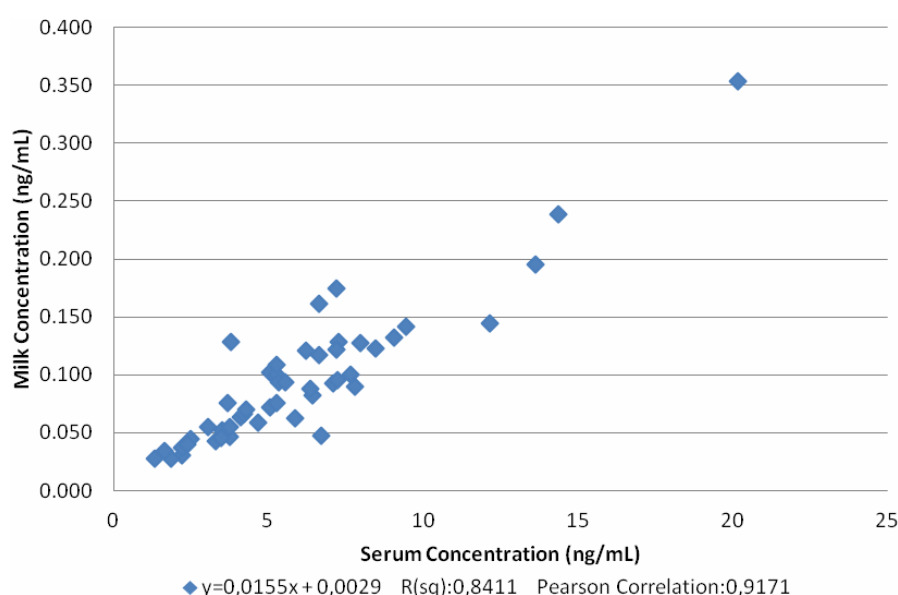


Figure 4.2.4: PFOS concentrations (ng/mL) in serum and milk samples from Sweden, 2004-2011. The linear equation of the line, including R^2 , is given together with Pearson's correlation coefficient.

4.2.3 Sampling and sample preparation methodology

The Global Monitoring Plan is using human milk and maternal blood as the two equally possible matrices for biological monitoring. The 2007 edition of the WHO protocol lists the criteria for selection of mothers, and these should be followed as closely as possible.

Sample matrices

Human milk

There are many factors explaining the variation in concentrations of POPs found in human milk (Harris *et al.* 2001; Loveday *et al.* 2002) and it is important to define selection criteria for the mothers to be included in the study (see selection criteria below).

The analyses of pooled human milk samples represent a cost effective method for comparing POPs levels between and within countries and to elucidate time trends. In the WHO Guidelines for Developing a National Protocol (WHO, 2007), provision is made for individual samples to be analysed for selected POPs (insecticide POPs and PCB 28, 52, 101, 138, 153, 180), in addition to the one (or perhaps two) pooled samples that will be analysed for all analytes.

Maternal blood

Maternal blood (plasma and serum) is used by AMAP, as the prime matrix to determine human exposure (AMAP, 2002). The majority of literature on human levels of POPs and other compounds of concern, have reported concentrations in human blood. Although it is an invasive procedure, in some cases it may be the matrix of choice, based on local infrastructure, customs and existing activities. As in the case for human milk, pooled samples can be used as a cost effective method for comparing POPs levels between and within countries and to elucidate time trends. Activities targeted at monitoring proteinophilic POPs such as PFOS are equally more likely to make use of blood as a preferred sampling medium. There seems to be a general trend that a growing proportion of hazardous compounds are more polar and may bind to proteins thus making blood the preferred medium in the future.

Experimental design

Human milk

Under WHO, a protocol has been developed for sampling and sample preparation methodology for exposure studies of Persistent Organic Pollutants (Malish & Moy, 2006; WHO, 2007). This protocol forms the basis for the human milk component of the GMP. An online version of the protocol is available at WHO Food Safety (see reference list) and is attached to this document as annex 4.

The State Institute for Chemical and Veterinary Analysis of Food (Germany) has met all the criteria for analyses of PCDD, PCDF, dioxin-like PCB, marker PCB and fat in human milk and was selected as a reference laboratory for the WHO exposure studies (WHO 2000, Malisch and van Leeuwen 2002)

The revised WHO protocol (WHO 2007) gives guidance on the number of samples/sampling locations and selection of donors. It also contains information on questionnaires, transport, storage, sample preparation and analysis. It contains annexes with questionnaires, summary information for a sample, an informed consent template, guidance for mothers, and an estimated timeline and budget. The WHO Research Ethics Review Committee has endorsed the project, but each country will also have to follow its own procedures. It should be noted that a country may have to adjust the volume to be collected per mother, if it does not intend to analyse individual samples.

Maternal blood

AMAP have in collaboration with Centre du Toxicologie de Quebec developed a protocol for sampling and sample preparation methodology for exposure studies on POPs. The protocol developed is the standard for all blood sampling procedures in AMAP. A detailed description of sampling, storage, shipping and analytical details is presented in annex 3, but the protocol is also available online at www.amap.no. A number of laboratories have met the requirements set by the AMAP Human Health Expert Group and are thus providing data for maternal levels of POPs within the AMAP network. Through the AMAP network additional information like standardised questionnaires are available.

The sampling guidelines for maternal blood of course have to be adjusted by the individual countries if there are additional plans for the use of the samples.

Number of samples/sampling location

The WHO guidelines (WHO, 2007) require samples from 50 individuals. However, current experience shows that some countries may not be able to recruit that many, and the proscribed collection period may therefore need to be extended to be able to collect 50 samples. Samples may also be collected from post-natal clinics.

The protocol also makes provision for a country to stratify the participants such that it represents the presumed exposure profile of each country. Elements that need to be considered here typically include diet, agriculture, occupational exposure, rural and urban residence, and proximity to potential POPs releasing industries or activities (such as waste sites). This stratification will need to be the same for following rounds, so that changes/trends can be followed. However, since the exposure profiles in most developing countries are not well characterized, assumptions need to be made, but these would have to be documented and form part of the information package. The protocol also makes provision for countries with adequate resources to submit two pooled samples. Although the protocol targets countries, it may be feasible that consideration for stratification, and even sample collection, could be done on a regional level. However, the effort should aim at the participation of as many countries and regions as possible, to enable a good baseline to be set.

Questionnaire and informed consent

The same questionnaire and approach should be applied for both milk and blood sampling. Information about the invasive nature of the procedure should be included. The informed consent template also needs to be considered in each country or region, and aligned according to local practice, custom and experience.

It is strongly recommended that the questionnaires developed in the WHO Guidelines for Developing a National Protocol be followed, but additional questions might be added if exposure profiles need to be better characterized. The questionnaires need to be translated into local languages, and administered by competent health or science professionals at pre-natal clinics or at collection. This is especially the case in developing countries, where some questions might need to be aligned with local knowledge and customs.

The first part of the questionnaire is intended to screen mothers during pregnancy. Some of the mothers will then be selected and notified. However, in many developing countries, means of communication might not support such an approach, and selection and recruitment may therefore have to be done at clinics or other centres, as appropriate.

Sample handling

The guidelines on handling of samples as laid down in the protocol should be strictly followed. Qualified personnel must be available to undertake the sampling and training may be required. If samples are to be stored in bio-banks special measures have to be taken in terms of sampling and sample handling and this is discussed in the section on specimen banking.

Human milk

Each of the 50 donors will contribute 50 ml of milk, of which 10ml is used for the pooled sample, 25 ml for individual analysis of basic POPs, and 15 ml stored for back-up and additional analysis, as may be required. During sampling of human milk from one mother the sample may be stored at 4 °C for a maximum of 72 hours. In countries where temperature control is not possible, the collection of milk samples should be done in bottles to which a tablet of potassium dichromate has been added. This method of preservation of the milk sample was applied successfully by some countries at the third round of WHO-coordinated exposure studies (van Leeuwen and Malisch, 2002; Schechter *et al.*, 2003).

When pooling samples from a number of mothers each sample must be heated to 38 °C and inverted gently several times to mix the cream layer. Thereafter a predetermined aliquot from each sample is pooled. The pooled sample is treated similarly and aliquots are divided into separate vials to minimize freeze-thaw cycle during analyses. The samples can be stored at -70 °C for an infinite length of time. When the sample is ready to analyze, it must be thawed and warmed to 38 °C. It can then be mixed by gentle inversion and the entire sample extracted. The container should be rinsed with solvents. Procedures for sample handling during storage, transport to analytical laboratory and handling by analyst etc. must be developed to take into account both cross-contamination by chemicals and transfer of disease between people.

Human blood

Sample handling is particularly important for obtaining homogeneous samples of human blood (plasma or serum) for analyses and to ensure sample integrity. Therefore, the guidelines on handling of samples as laid down in the protocol should be strictly followed. Qualified personnel must be available to undertake the sampling and training may be required.

Conditions of sample handling after sampling: the current protocol states that plasma samples can be kept for 5 days at room temperature. At high ambient temperatures (*i.e.* the tropics), samples should not be stored for longer than 1 day before being frozen, and be kept out of sunlight.

When pooling is required, 5 ml of each plasma sample is added, for a total of 250ml. Pooled samples can be stored at -70 °C until analysis. It can then be thawed to room temperature, be mixed by gentle inversion and the entire sample extracted. The container should be rinsed with solvents. Procedures for sample handling during storage, transport to analytical laboratory and handling by analyst etc. should take into account the prevention of both cross-contamination by chemicals and infections.

Lipid adjustment of blood and breast milk contaminant data

Since there are many factors that may affect the composition of human milk (Harris *et al.*, 2001; Harris *et al.*, 2002; Lovelady *et al.*, 2002), note should be taken of the guidance in the Fourth WHO-Coordinated Survey (WHO, 2006).

Lipid levels in breast milk are approximately ten times higher than lipid levels in blood. Lipid normalization (equal concentrations of lipids) allows concentrations of lipid soluble compounds such as POPs in maternal blood and breast milk to be more easily compared.

Lipid levels in blood vary with meals, but lipid adjustment has been shown to adjust for the effect of meals on lipid soluble contaminants such as POPs (Philips *et al.* 1989). For more information on lipids, consult Philips *et al.* (1989) Lipid levels in maternal blood have also been shown to increase during gestation, rising to a maximum just before delivery and declining to baseline values shortly after delivery (Longnecker *et al.* 1999). Hansen *et al.* 2010, recently showed that lipid adjustment for the varying levels during pregnancy allowed the best normalization of the data. For blood plasma, an enzymatic determination of the lipids is required, and the use of an appropriate summation formula.

Ethics

Each country will have to ensure that their protocols be approved by the relevant, ethical committees. Evidence of such approval should accompany the information package.

The revised WHO protocol (Malish & Moy, 2006; WHO, 2007) has been endorsed by the WHO Research Ethics Review Committee.. Any variation from the protocol, based on local ethical considerations, should be noted, and this should be included in the information package that accompanies the samples. Evidence of such approval should accompany the information package.

HIV/AIDS

All human biological samples shall be treated as if these are infected in order to reduce the chances of infecting personnel.

Transporting of samples

Shipping of milk and blood samples to the selected analytical laboratories should be done in accordance with relevant protocols, and any appropriate instructions given by the responsible receiving party. Given the general prevalence of HIV and other infective diseases such as hepatitis, human milk and blood samples should be labelled and handled as appropriate, as a precautionary procedure.

Interlaboratory comparison and cooperation issues

The AMAP ring test for persistent organic pollutants is organized through the Centre de Toxicologie du Québec / INSPQ. As for details, see the website (<http://www.ctq.qc.ca>) and the External Quality Assessment Scheme (G-EQUAS), Germany. All laboratories willing to be included will be offered cooperation regarding methodological issues, references materials, cross checking of samples, handling of data etc. under strict security rules.

To ensure reliability and improve comparability, WHO has routinely carried out inter-laboratory analytical quality assurance studies of POPs. WHO has also carried out proficiency studies for POPs (insecticide POPs and PCB 28, 52, 101, 138, 153, 180) in human milk.

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WHO Food safety: <http://www.who.int/foodsafety/chem>

4.3 Water

4.3.1 Introduction

Water concentrations of POPs in large lakes, coastal seas, and open oceans, reflect a dynamic balance of inputs via rivers and atmospheric deposition as well as re-release from sediments, and removal pathways such as volatilization and sedimentation (Jurado et al. 2007; Stemmler and Lammel 2009). Long-term data on POPs in water thus provides important information that can be used to assess the effectiveness of measures taken to reduce emissions. Concentrations of POPs in surface water are directly linked to their bioaccumulation in the food-chain (Thomann et al. 1992; Borgå et al. 2005); hence knowing dissolved concentrations in the water enables prediction of concentrations in aquatic species using bioaccumulation factors or lipid-water partitioning and food web biomagnification models (Gobas et al. 2009).

With the addition of water-soluble POPs such as PFOS and HCH isomers to the Stockholm Convention and the possible addition of others such as endosulfan, consideration needs to be given to including water as a recommended matrix in the Global Monitoring Plan for POPs. Global and coastal ocean waters, and large lake waters, represent a major sink for PFOS and HCHs and to a lesser extent for other POPs. These systems could also represent a source of POPs emissions to the atmosphere as a result of declining air concentrations and climate change *e.g.* reduced ice cover, increased water temperatures (Hung et al. 2010; Nizetto et al. 2010).

Awareness is growing that transport via ocean currents may be an important pathway for persistent chemicals to reach polar and other remote regions, especially for the more soluble substances (Gouin and Wania 2007; Armitage et al. 2009). As discussed in Section 4.1.1 on characterization of transport, CTDs have been calculated for POPs discharged into water as well as to air. Water CTDs tend to be much shorter than for air due to slow degradation and volatilization rates for semi-volatile compounds. As noted previously these distances should be compared only in a relative manner and are dependent on model parameterizations. PFOS as well as hydrophilic OCPs such as HCH isomers, have longer CTDs in water compared to PCBs or PCDD/Fs due to lack of removal via sedimentation, as well as limited volatilization and slow degradation. In fact, PFOS and PFOA have been proposed as chemical tracers of global circulation of ocean waters (Yamashita et al. 2008).

Water has become a widely used environmental matrix for monitoring POPs, particularly for the chlorinated pesticides, despite challenges related to collecting samples and determining trace levels. The availability of environmental quality standards expressed in terms of concentrations in water (EQSs;(European Commission 2006)), guidelines (EQGs;(Environment Canada 2002)), ambient water quality criteria (US EPA 2009), and peer reviewed literature on thresholds for effects on aquatic biota (*e.g.* No observable effect concentration (NOECs); lowest observable adverse effects) is a major driver of continuing interest in these measurements as part of risk/exposure assessments (Lepom et al. 2009). EQSs, EQGs, AWQCs, and NOECs are available for most of the chemicals on the POPs list, although generally for the parent chemical and not for degradation products.

Data on concentrations of some POPs, such as PBDEs and PCDD/Fs in surface waters are very limited. PCBs and organochlorine pesticides (OCPs) such as DDT have been included in surface water monitoring programs for many years. However, among the 22 POPs, HCH isomers which are relatively water soluble compared most other chlorinated and brominated POPs (Annex 6), as well as PFOS, have been determined more widely. Concentrations of α -HCH ranged from 5-700 pg/L (Lakaschus et al. 2002) and PFOS from <10-590 pg/L (Ahrens et al. 2009) in the Atlantic Ocean. By contrast PCB concentrations (sum 7 congeners) are in the range of 0.07 to 1.7 pg/L (Gioia et al. 2008). Long term water monitoring programmes have been set up mainly in developed regions in the northern hemisphere, in particular where regional environmental programmes with a focus on the marine environment are in place (OSPAR, HELCOM, Mediterranean., Caspian, Black Sea) (Annex 7). There are also recent reports for many other regions such as in African lakes (Kasozi et al. 2006) and rivers in India (Sankararamakrishnan et al. 2005; Malik et al. 2009). Annex 7 lists sampling programs and selected individual investigations for POPs in water that were reported in UNEP persistent toxic substances (PTS) reports (UNEP 2003).

4.3.2 Experimental design

Chemicals selected for water monitoring

PFOS (anion) is recommended for water monitoring under the GMP based on the proven ability of numerous investigators to determine it in water and the availability of standard methods. Given the challenges of determining PFOS anion in air (see section 4.1.1) water represents the best environmental matrix for monitoring PFOS. HCH isomers can also be determined relatively easily by many investigators, however, substantial data exists for them in air and another matrix is not essential for evaluating effectiveness of the Convention. Determination of other POPs in water is generally much more challenging, particularly for PBDEs and PCBs, due to order of magnitude lower concentrations combined with greater quality control issues such as contamination from lab and ship air, and the need for large volumes to achieve levels above method detection limits. Nevertheless the discussion of study design assumes that a range of neutral POPs might be analyzed in water along with PFOS.

Sampling sites

The objective of the proposed water sampling network is to obtain representative data for assessing time trends at selected background sites. The data would also be used to assess exposure of aquatic food webs, and the transport of POPs in regional seas and in the Oceans. Similar to air monitoring we interpret 'representative' as being a sufficient number of sampling sites to make general conclusions about spatial and temporal trends of POPs and not to be representative of heterogeneity of a particular region. Determination of POPs in ground waters or in drinking water is also not envisioned here. However, a series of sites generating data on background levels of POPs in surface waters could complement more dense national or regional sampling networks in freshwater and marine environments.

Initially, for addressing POPs trends in water, the GMP should in each region:

- Select appropriate water bodies *e.g.* large lakes (> 10 km²) or seas, and open ocean sites if feasible (*e.g.* part of regular oceanographic cruises); 3 to 5 stations within each UNEP region
- collect large volume samples using resin or polyurethane foam extraction columns ;
- Consider deployment of passive water sampling technologies; co-locate passive water sampling stations with the large volume collection stations
- Co-locate where possible water sampling near air sampling stations (*e.g.* with GAPS) in order to estimate air-water exchange of POPs

Siting considerations

As discussed for air sampling the sampling sites need to be sufficiently remote from urban centres, harbors, and industrial waste water inputs, and other sources of POPs, as to reflect concentrations typical of a large area around the site.

Requirements for water sampling sites include:

- ease of access by limnological or oceanographic vessels with capacity to deploy water sampling equipment
- presence of an existing routine sampling program with water chemistry data
- availability physical measurements (temperature, pH, conductivity), flow (*e.g.* outflow from a lake)
- meteorological observations
- personnel who could be trained in the sampling techniques.
- Availability of suitable laboratory facilities to prepare sampling media and subsequently extract and analyse the samples

Regional decisions on site selection will necessarily include consideration of existing programs. Water Monitoring Programmes targeting POPs and related PTS are listed in Annex 7. No global programs for POPs in water currently exist. The UNEP Global Environment Monitoring System GEMS

(<http://www.gemswater.org/>) has been working on a compilation of monitoring data for water. The GEMS database includes information on water quality from 106 member countries.

If lakes in populated areas are used because they are part of existing programs, then sampling of open lake waters, as remote as possible from river or waste water inflows, is recommended. Sampling of isolated lakes with limited or no human activity *e.g.* mountain lakes, would provide information on true background contamination. Sampling of river waters is not recommended due to variation with flow, suspended solids levels, proximity to legacy sources etc. For coastal countries, off shore (outer coastal) ocean waters are recommended. For national programs which include capacity for ocean cruises and on board water sampling, collection of water at standard (near surface) depths along standard cruise transects including, if possible, mid-ocean locations. A network of stationary sites sampled annually in coastal waters and large lakes would, if maintained over many years, provide temporal trend data while oceanographic cruises would provide information on ocean transport and global fate.

Sampling frequency

Consideration needs to be given on how frequently to sample. POPs concentrations in water may vary seasonally due to seasonality in phytoplankton and particulate organic matter, and other factors affecting inputs such as precipitation, runoff etc. Seasonal cycles in water concentrations of POPs has been found in ocean waters in the Canadian Archipelago (Hargrave et al. 1997; 2000). In general the frequency of sampling will probably be dictated by the characteristics of the water body and the time dependence of loadings.

4.3.3 Sample Collection

1. Introduction

A wide range of water collection methodology has been employed for obtaining samples for POPs analysis, ranging from hand dipping of 1L bottles to *in situ* submersible samplers collecting hundreds of liters. As noted in Chapter 5, it is difficult to give general recommendations as they will depend significantly on study objectives and local capacity. Standard operating procedures for selecting sites, cleaning equipment, and avoiding contamination, *e.g.* by use of “clean hands/dirty hands” protocols are available from USGS (2006) with a focus on rivers and streams. The European Commission (2007) and ISO(2006) provide practical guidance for sampling of contaminants in freshwaters. HELCOM (2006a; 2006b) offers useful advice on marine sampling design including seawater collection.

Sampling depths in the range of 1 to 10 m are recommended. This is a practical range of depth based on use of ship intakes and on-board pumping systems. Niskin or Glo-flo type samplers can be used for deeper depths, and depth profiles, however, there is potential for wall effects (contamination, sorption) particularly with small volumes (Wells 1994; Petrick et al. 1996). Adsorption losses can be evaluated using spikes of surrogates added to sample containers or to oceanographic bottles once they have been brought to the surface. Actual depths will depend on the characteristics of the waterbody. Care should be taken to avoid sampling the surface micro layer because it could have higher levels of contamination due to the presence of particulates, lipids and hydrocarbons (Wurl et al 2006).

Assuming sampling of background sites is the main goal of a GMP for water, then the number of sampling techniques that can realistically be applied in order to achieve adequate limits of detection above blanks is limited. The techniques available are either (1) pumping water through solid phase media (C18 disks or columns, XAD resin, or polyurethane foam or (2) passive sampling with SPMDs (Semi-permeable membrane device), silicon rubber or polyethylene plastic sheets. A major exception is in sampling for PFOS (discussed below).

2. Active systems, solid phase media and filtration

Direct pumping thru a filter into a column holding the solid phase media has been widely employed in studies of POPs including HCH isomers in remote lake and ocean waters (Lakaschus et al 2002). There are many variations of this including the use of *in situ* samplers which are programmed to turn on and off underwater, and in line systems bringing seawater directly into clean rooms on ships. There have been several recent investigations of the performance of various solid phase media for extracting hydrophobic organics from surface waters. A multi-investigator study led by the European Commission Joint Research Centre (ECJRC) showed that PBDEs and PAHs could be determined adequately in

natural water by a wide range of sampling and analytical methods.. A key issue identified in the ECJRC study was partitioning between particles suspended in the water body. The recommendation from this latter study, and in European guidance (European Commission 2007) was to separate suspended particulate matter (SPM) from the water using appropriate filtration so that a “so-called” dissolved phase, operationally defined as contaminant that passes a 0.7-1 µm glass fiber filter (GFF), was analysed separately.

Solid-phase extraction (SPE) cartridges have been widely used to extract relatively small volumes (1–5 L) for OCP analysis. They also have the advantage of being performed in the field with simple portable pumping equipment (Zuagg et al. 1995) and other media such as divinylbenzene solid-phase disks have been shown to outperform XAD resins for OCP and PCB extractions of filtered water (Usenko et al. 2005).

3. Sampling for PFOS

PFOS and related perfluoroalkyl compounds (PFCs) are water soluble and have relatively low sediment-organic carbon partition coefficients compared to neutral halogenated compounds on the POPs list (Annex 6). Thus the PFCs are preferentially found in the dissolved phase in surface and ground waters. PFOS and other PFCs are readily detected in all surface waters at pg/L to ng/L. There have already been a large number of surveys of PFOS and other PFCs in rivers as well as measurements in all the major world oceans (Yamashita et al. 2008; Ahrens et al. 2009a). Collection of seawater samples has been done through ship intake systems (Ahrens et al. 2009a) and via Niskin bottles (Yamashita et al. 2004) into plastic or glass bottles. In lakes and large rivers, direct pumping into sampling bottles (Furdui et al. 2008) and collection from Niskin type samplers (Scott et al. 2009; Scott et al. 2010) and from ship intakes (Ahrens et al. 2009b) has been used. Samples for PFOS analysis have generally not been filtered prior to extraction. A recent study of waters in the Elbe River (Germany) and the North Sea indicated that on average 14% of PFOS was in the particulate phase (Ahrens et al. 2009b). In ocean waters PFOS was not detectable on particulates (Ahrens et al. 2009a) likely because of the lower SPM and thus filtration is not recommended, unless it can be done with an inline system or in a clean room (Ahrens et al. 2009b) because it could introduce contamination. Contamination is also introduced from polytetrafluoroethylene (PTFE) materials due to the use of perfluorooctanoate (PFOA) as a processing aid for PTFE production. Common sources are PTFE tubing, o-rings and other seals. PTFE bottles or bottles with fluorinated interior coatings and these should be avoided.

4. Passive sampling

Stuer-Lauridsen (2005), Vrana et al. (2005) and Booij (2009) have thoroughly reviewed the history and use of passive samplers in POPs monitoring in the aquatic environment. Passive sampling offers an alternative for widespread monitoring of hydrophobic POPs in water. Most POPs have log K_{ow} and Log K_{oc} of $10^4 - >10^6$ (Annex 6) and thus preferentially partition to organic surfaces. Semi-permeable membrane device (SPMDs), consisting of low density polyethylene (LDPE) tubing filled with triolein, were originally developed to determine bioavailable concentrations of POPs in water (Huckins et al. 1990; Lu et al. 2002) and remain widely used for hydrophobic organics. Single-phase polymeric materials, such as LDPE strips (Adams et al. 2007), polyoxymethylene (POM) (Jonker and Koelmans 2001), and silicone (Mayer et al. 2000; Booij et al. 2002; Rusina et al. 2007) are increasingly being used. Passive samplers measure chemical activity of pollutants, the concentration in the dissolved phase, and cannot be compared directly with EQSs, WQGs and AWQCs, which are based on whole water concentrations, even though the fraction sampled is more toxicologically relevant (Allan et al. 2009).

Passive sampling is based on the diffusion of analyte molecules from the sampled environmental medium (water) to a receiving phase in the sampling device. The diffusion occurs as a result of a difference between chemical potentials of the analyte in the two media. The net flow of analyte molecules from one medium to the other continues until equilibrium is established in the system, or until the sampling is stopped. The mass of chemical sorbed in the sampler following a given exposure period is initially proportional to the time-weighted averaged (TWA) concentration in the environmental medium to which the sampler was exposed (integrative samplers) and subsequently once equilibrium is achieved to the concentration in the environmental medium with which the device is at thermodynamic equilibrium (equilibrium samplers).

The main advantage of kinetic or integrative sampling is that even contaminants from episodic events commonly not detected with spot sampling are collected by the sampler. This permits the measurement of TWA contaminant concentrations over extended time periods using a single sample (extract from the passive sampler). This gives a more representative picture of contaminant levels than that obtained with the use of infrequent spot samples of water.

Passive samplers effectively sample large volumes of water (up to several thousand litres) when deployed for several weeks to months (Lohmann and Muir 2010) and are therefore time-integrating unlike samples collected by “active” systems. Allan et al. (2009) compared several passive devices (including LDPE, silicone and SPMDs) and liquid-liquid extraction for *p,p'*-DDE and PAHs, PCBs and hexachlorobenzene and concluded:

1. passive samplers provide data that are less variable than that from “whole water” sampling since the latter may be strongly influenced by levels of suspended particulate matter.
2. Detection limits are much better with passive samplers due to high sampling rates and sampler/water partition coefficients.
3. While all passive devices performed well LDPE samplers were found to be the most reproducible.
4. Linear uptake is observed for the more hydrophobic contaminants during exposures of up to one month
5. Despite different modes of calculation, relatively consistent TWA average concentrations are obtained for the different samplers
6. Bio-fouling induces only minor changes in estimates of TWA concentrations.

The period of time of deployment is an important consideration for passive samplers. There exists a trade-off between longer deployment periods to maximize uptake of POPs while limiting biofouling in the field. During their deployment, passive samplers integrate dissolved concentrations over time, until equilibrium is reached. Time to equilibrium is chemical-specific for different sampler types and dependent on the sampler-water partition coefficient values *i.e.* sorptive capacities for particular chemicals. Passive samplers can either be deployed as equilibrium samplers or in the linear uptake phase. For the various POPs, times to reach equilibrium will vary dramatically between *e.g.*, the HCHs and DDTs. The long deployment periods that are still adequate for integrative sampling of very hydrophobic compounds ($\log K_{ow} > 6$) such as DDT will result in equilibrium sampling of less hydrophobic compounds. This means that the sampler might not reflect TWA concentrations of less hydrophobic POPs if it is exposed for extended time periods.

Calculation of sampling rate and water concentrations with passive samplers: For devices that operate in the linear or integrative mode (Figure 4.3.1), the sampling rate is given by the product of the overall analyte mass transfer coefficient and the active surface area of the sampler ($R_s = k_o A$). Sampling rate may be interpreted as the volume of water cleared of analyte per unit of exposure time (*e.g.* L day⁻¹) by the device and is independent of the analyte concentration in the sampled medium. It can be affected and modulated by the analyte diffusion and partition properties in the media along the diffusional path (water boundary layer and polymers), and is determined in laboratory calibration studies.

Often the main barrier to mass transfer is the water boundary layer (WBL) located at the external surface of the sampler. In such a case the sampling rate is significantly affected by environmental variables such as water temperature, turbulence and biofouling. If laboratory calibration data is to be used for calculation of TWA concentrations, the effect of these variables has to be either controlled or quantified. Performance reference compounds (PRCs) must be added to help understand if the sampler is approaching equilibrium and the degree to which environmental variables such as temperature, turbulence and biofouling affect the sampling kinetics (Huckins et al. 2002). The measurement of PRC dissipation provides information on contaminant exchange kinetics between water and the sampler. Use of multiple PRCs with a range of $\log K_{OW}$ makes it possible to establish when kinetics of uptake into the sampler are membrane- or boundary layer-controlled. Amounts of analytes absorbed by the samplers follow a first-order approach to equilibrium

$$N = K_{SW} \cdot V \cdot C_{TWA} \cdot [1 - \exp(-k_e \cdot t)]$$

where N is the amount of analyte absorbed (ng), K_{SW} = sampler-water partition coefficient ($L L^{-1}$), V = volume of the sampler (L), k_e = exchange rate constant (h^{-1}), t = exposure time (h), and C_{TWA} = time weighted average concentrations $ng L^{-1}$. PRC dissipation also follows first-order kinetics:

$$N_{PRC} = N_{0,PRC} \cdot \exp(-k_e \cdot t)$$

where $N_{0,PRC}$ and N_{PRC} are PRC masses in the samplers prior to and following exposure, respectively and where k_e is given by:

$$k_e = R_s / K_{SW} \cdot V$$

where V the volume of the sampler (L) and R_s the analyte uptake rates ($L d^{-1}$).

Equilibrium sampling (Figure 4.3.1) can be achieved through the use of thin membranes, in which POPs display high diffusivities, as often used in contaminated sediments and harbours. After equilibrium has been obtained in the field, dissolved concentrations are simply obtained by dividing the POP concentration in the passive sampler by its passive sampler-water partitioning coefficient.

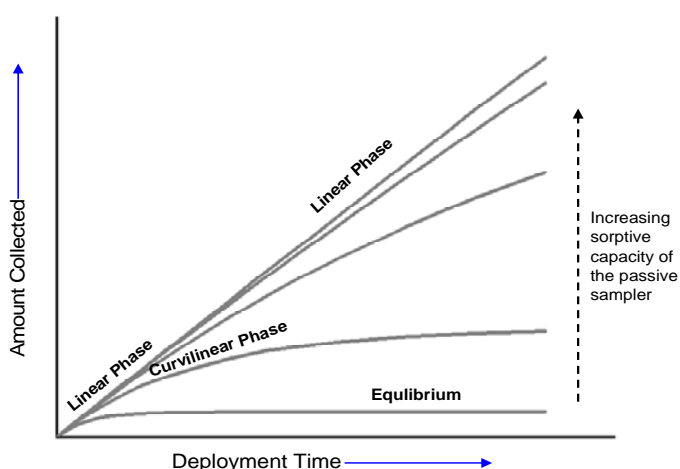
$$C_{TWA} = C_{PS} / K_{SW}$$

Where C_{PS} is the concentration in the passive sampler ($ng L^{-1}$ or $ng g^{-1}$).

The use of passive samplers for field-measurement of POPs in open lake or seawaters remains uncommon, despite their attractive characteristics (Stuer-Lauridsen 2005). Cornelissen et al. (2008) used polyoxymethylene (POM) samplers to determine dissolved PCDD/Fs and PCBs in the open Baltic Sea for 154-192 days. This deployment time enabled detection of PCDD/Fs at pg/m^3 concentrations in water. Roach et al (2009) also demonstrated the sub pg/L detection of SPMDs for PCDD/Fs in Sydney harbour including some outer harbour locations and Morgan and Lohmann (2008) determined dissolved PCBs in outer Narragansett Bay (RI) using LDPE samplers. Booij et al.(2006) summarized and analysed POPs monitoring data obtained by SPMDs, silicone sheets and mussels in the Scheldt-North Sea area over the last decade to understand the similarities and differences between these sampling matrixes. However, most passive sampling devices, particularly SPMDs, have generally been deployed much more extensively in rivers and harbours and to estimate pore water concentrations in sediments (Stuer-Lauridsen 2005).

Passive samplers are generally deployed in stainless steel cages or frames attached to moorings so that their position in the water column is maintained (Cornelissen et al. 2008). Deployment at background sites, as envisioned for the GMP for water, is challenging since permanent moorings are needed. Lohman and Muir (2010) have suggested making use of existing monitoring buoys in key locations such as the Great Lakes, and other major lakes and seas, as well as in outer coastal areas. The major requirement for a given site is that it should be away from a major point source, and temperature (and salinity, where appropriate) data need to be available for the deployment period.

Figure 4.3.1: Illustration of uptake of POPs from water by a passive sampler. Samplers can operate in the linear phase generally over shorter deployment times and depending on film thickness and the hydrophobicity of the chemical. With thin films that have lower capacity, samplers can also achieve equilibrium for some chemicals



4.3.4 Analytical considerations

1. Background contamination

As discussed for air sampling media, the sorbents such as XAD resin and PUFs are pre-cleaned by sequential Soxhlet extraction using a combination of polar and non-polar solvents (*e.g.* acetone: hexane and/or acetone followed by hexane) prior to use in extraction columns. Prepackaged media such as C18 disks and solid phase cartridges are conditioned by elution with a polar and non-polar solvent combination in the analytical laboratory or (if conditions permit) in the field prior to use (Jantunen et al. 2004; Usenko et al. 2005). Glass fiber filters must also be baked (350 °C) prior to use and stored in a sealed container.

Additional precautions for solid phase sampling systems are (1) field blanks consisting of the same media that are attached temporarily to the pumping system during the sampling period (2) procedural blanks prepared at the same time as the field blanks and held in the laboratory. Comparison of the field and procedural blanks permits and assessment of contamination during sampling (Castro-Jiménez et al. 2010). The same approach is used for passive samplers. Field blanks are exposed to air for the same time as the deployed samplers allowing comparison with procedural blanks held in the laboratory (Adams et al. 2007; Roach et al. 2009).

2. Extraction procedures

Details on the extraction of POPs from solid phase sampling media including passive samplers are provided here. Following extraction the samples can be analysed quantitatively by methods described in Chapter 5. In most cases fractionation of the extracts on silica or Florisil (Sect 5.2) is required for analysis of HCH isomers prior to GC-MS analysis in order to remove non-volatile co-extractives.

The elution of reverse-phase or XAD resin water sampler cartridges generally involves the use of a water-miscible solvent (usually methanol or acetone) first to remove water followed by a solvent of intermediate polarity such as DCM, methyl *t*-butyl ether or ethyl acetate. Combined extracts are then partitioned into hexane (Smith and McLachlan 2006; Castro-Jiménez et al. 2010). Other investigators have directly extracted media without removing residual water (Sobek et al. 2003) and removed water with a Dean Stark apparatus or by pipet (Jantunen et al. 2004).

Solid-phase media such as Speedisks and SPE cartridges are eluted with medium polarity solvents such as DCM (Jantunen et al. 2004; Usenko et al. 2005) as per manufacturer's recommendations. Residual water in the eluate is removed by pipet and the extracts are further dried with sodium sulfate that had been baked at 400 °C.

Breakthrough of target analytes on XAD or PUF is generally monitored using secondary columns (Castro-Jiménez et al. 2010). Recovery surrogates (usually mass labeled standards) are added prior to the extraction step. In addition some investigators add standards to resin columns prior to deployment (Ueno et al. 2007; Zarnadze and Rodenburg 2008).

Liquid-liquid extraction of OCPs water has been used in some recent studies (Lafrenière et al. 2006; Wurl et al. 2006; Malik et al. 2009). However other studies have come out against liquid-liquid extractions at background sites due to potential for contamination from lab air, difficulty of separating particle and dissolved phase, solvent disposal concerns, and poor performance compared to solid phase methods (Zuagg et al. 1995; Petrick et al. 1996; Hanke et al. 2007). Liquid-liquid extraction may be suitable in certain situations particularly where HCHs are the main POP of interest (Wurl et al. 2006). Another large volume application uses liquid:liquid extraction in a continuous flow approach allowing larger samples to be extracted (Neilson et al. 1988; Lafrenière et al. 2006).

PFOS and other PFCs are extracted from water with weak anion exchange (WAX) solid phase cartridges (ISO 2008; Taniyasu et al. 2008). The cartridges are preconditioned by elution with 0.1% NH₄OH in methanol, and then methanol and (precleaned) water. Sample cartridges are eluted with 25mM ammonium acetate buffer (pH 4) and the target analytes then eluted with 0.1% NH₄OH in methanol (ISO 2008; Taniyasu et al. 2008). Water volumes of 0.5-1L are sufficient for pg/L measurements of PFOS. In general no further cleanup of extracts for PFOS is required and samples can be submitted for LC-tandem MS analysis (see *Chapter 5*).

Single phase passive samplers such as LDPE, POM and silicone strips are wiped with a damp paper tissue to remove biofilms and then extracted with pentane (Allan et al. 2009), hexane (Cornelissen et al. 2008) or DCM (Morgan and Lohmann 2008). At this stage sample extracts may be suitable for GC analysis although additional cleanup may be required particularly for PCDD/Fs (Cornelissen et al. 2008). Two phase passives such as SPMDs are dialysed with hexane (Huckins et al. 1990). Residual triolein is removed from the extract through a size-exclusion chromatographic column with DCM as the mobile phase (Allan et al. 2009; Roach et al. 2009).

4.3.5 References

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5 ANALYTICAL METHODOLOGY

5.1 Sampling

The aim of any sampling activity is to obtain a sample that can serve the objective of the study. In this activity it is considered indispensable to ensure the representativeness and integrity of the sample during the entire sampling process. Additionally, quality requirements in terms of equipment, transportation, standardization, and traceability are indispensable. It is important that all sampling procedures are agreed upon and documented before starting a sampling campaign.

The analyte, matrix, sampling site, time or frequency, and conditions should be determined depending on the objective of the sampling. Detailed guidance on sampling for air, human milk/blood and water are given in Section 4.1.1, 4.2.3 and 4.3.2, respectively. In case of human samples it may also be necessary to use a suitable interview form and prior to sampling obtain ethical clearance from relevant authorities.

Although it may be too expensive to get full accreditation for sampling, Quality Assurance and Quality Control (QA/QC) procedures for sampling should be put in place.

5.2 Extraction and clean-up

The appropriately prepared sample can be extracted by any of a number of techniques. The main points to consider are to allow adequate time of exposure of the solvent system in the sample matrix and to limit sample handling steps, *i.e.*, avoid filtration steps by using Soxhlet or semi-automated systems (*e.g.*, pressurized fluid extractors, EPA method 3545A). Extractions can also be accelerated by the use of ultrasonication. Cross contamination from residues left behind by high levels of POPs in other samples is a concern at this stage and equipment must be thoroughly cleaned and checked from batch to batch.

Purity of extraction solvents is also a major consideration. Only high purity glass distilled solvents should be used. Internal standards should be added to the sample as early as possible in the process.

If the results are reported on a lipid weight basis, the determination of the lipid content in the sample is critical. From this aspect the choice of solvents is crucial, and has been discussed in the literature (Jensen et al., 2003). If the whole sample is not used for the extraction, the remaining part can be frozen and stored for future control analysis, or analysis of other substances. Likewise the extracts not used in the analysis can be stored, preferably in glass ampoules, at -20 °C.

Isolation steps can be relatively straightforward for low lipid samples such as air. Generally small silica gel or Florisil columns (either prepared in the lab or pre-purchased) will suffice. The purpose of this step is to remove co-extractive interferences and to separate non-polar PCB (plus HCB and 4,4'-DDE) from more polar POPs (HCH, most chlordanes, dieldrin/endrin). This is achieved by applying the extract in a small volume of non-polar solvent and fractionating by eluting with hexane or iso-octane followed by one or two other elutions of increasing polarity. Alumina is not recommended because of possible dehydrochlorination of some POPs, *e.g.*, 4, 4'-DDT.

For the human samples, a lipid removal step must be included. This can be achieved using size exclusion or gel permeation chromatography (GPC) either in automated systems, using high pressure liquid chromatography (HPLC) columns or by gravity flow columns. The advantage of GPC is that it is non-destructive while the disadvantage is a requirement for large volumes of solvent (low pressure or gravity systems) or expensive columns (HPLC). Lipid removal using sulfuric acid washing or sulfuric acid – silica columns is also effective but does result in loss of some analytes such as dieldrin. A suitable, simple option is to use (basic) alumina columns and elute these with pentane. They have a high capacity for fat removal (higher than silica or Florisil). After this step or after fractionation a concentrated sulphuric acid treatment, *e.g.*, by shaking, helps to make the extract very clean. Unfortunately, dieldrin and endrin are not resistant against such a treatment and should be determined before the extract is treated with sulphuric acid.

Following fractionation on silica or Florisil final extracts are transferred to (syringe standard) small gas chromatography (GC) vials for analysis. Addition of a recovery standard to check solvent volume is recommended at this stage. Careful evaporation is required at this step and only high purity compressed gas (usually nitrogen) should be used.

Analytical methodology for PCDD/PCDF and dioxin-like PCB differs from that used for routine indicator-PCB and OCPs in that it requires much lower detection limits (typically 10-100 times lower) because they occur at very low concentrations and guideline limits in food or feedingstuffs are in the low pg/g or ng/kg or range per sample; the Provisional Tolerable Monthly Intake is 70 pg/kg body weight (Joint FAO/WHO Expert Committee on Food Additives (JEFCA), 2001). To enforce and control these low concentrations for PCDD/PCDF isotope dilution MS (use of ^{13}C -surrogates for all PCDD/PCDF homologue groups), enrichment on carbon to isolate planar compounds, very small final volumes (10 μL -50 μL) for GC-HRMS quantification is used. Methodology for PCDD/PCDF, slightly modified to include the dioxin-like PCB, developed by the US EPA (method 1613), is well established and validated by numerous inter-laboratory comparisons. This methodology would be recommended for use in a global monitoring programme. This very specific guidance for the extraction, isolation and quantification of PCDD/PCDF is recommended in order to be in compliance with ongoing programmes and compatible with results generated with these methods over the past ten years.

Methodology for determination of PFOS in human blood, air and water differs from that used for the other POPs because of the unique properties of the perfluorinated chemicals (PFCs). An International Council for Exploration of the Sea (ICES) "Techniques" article by Ahrens et al. (2010) provides detailed guidance for determination of PFOS and related anionic compounds, as well as a PFOS precursor, perfluorooctanesulfonamide (PFOSA), in water. Van Leeuwen and deBoer (2007) provide a detailed review of the extraction and isolation of PFOS and PFOSA from water and blood and also discuss sampling and analysis of the volatile precursors (perfluorooctane sulfonamido alcohols, PFOSE and) in air.

In blood, PFOS and its major precursor, PFOSA, are usually extracted using weak anion exchange (WAX) solid phase cartridges. Red blood cells are precipitated using acetonitrile or formic acid to prevent clogging of the SPE column (Taniyasu et al. 2005; Kuklenyik et al. 2004;2005). Several isolation approaches for PFOS related compounds have been used at this stage and there is currently no accepted standard method. Taniyasu et al. (2005) used centrifugation to remove precipitated proteins and then combined the supernatant with 0.01N KOH in methanol followed by shaking for 16 h. This solution is diluted with water and passed through a WAX column to isolate the PFCs. Elution with methanol recovers non-anionic PFOS related compounds including PFOSA, while PFOS was eluted with 0.1% ammonia in methanol. The weak alkaline digestion was shown to improve recoveries compared to the widely used ion-pairing extraction method (Hansen et al., 2001. Kuklenyik et al. (2004; 2005) reported good recoveries of PFOS, PFOSA and a range of perfluoroamido alcohols and their metabolites (2-(N-methylperfluorooctanesulfonamido) acetic acid) from blood serum, following protein precipitation with formic acid, using a "hydrophilic-lipophilic balance" (HLB) SPE column.

Although various approaches have been used the results of the first international interlaboratory study on PFOS and related compounds in human samples showed a good comparability of the different methods applied by the participants as 61%–73% of the participants had satisfactory z-scores for PFOS and PFOA in blood and plasma (Van Leeuwen et al. 2006).

Guidance for extraction of PFOS and related PFCs from water has been provided in Section 4.2.2 and Ahrens et al. (2010) For water an ISO method has been developed (ISO 2008) in which PFOS and other PFCs are extracted from water with weak anion exchange (WAX) solid phase cartridges. However, this method has a limit of quantification of 10 ng L^{-1} only, whereas for environmental samples such as sea water typically contains concentrations at pg L^{-1} levels. As described for blood serum, the PFCs are then eluted from the cartridges in two fractions. The first fraction is methanol and contains PFOSA and other neutral PFCs, whereas the second fraction is obtained with 4 mL of 0.1 % ammonium hydroxide in methanol and contains the PFOS. In general no further cleanup of extracts for PFOS is required and samples can be submitted for LC-tandem MS analysis as discussed below. Where cleanup of water extracts is required due to co-extractive materials interfering with chromatography or suppressing ionization in the mass spectrometer, Ahrens et al. (2010) recommend the use of a carbon column cleanup with ENV CARB cartridges. The PFCs are generally not absorbed by the carbon whereas lipophilic and pigmented co-extractives are usually retained.

A critical feature of all methods for PFCs that employ LC-MS/MS is the use of ^{13}C - and/or $^{18}\text{O}_2$ -labelled PFOS and PFOSA substances from the extraction step. The isotope-dilution technique, which uses isotope-labeled internal standards chemically identical to the analytes of interest, corrects for the

matrix effects on the analytes recovery during the extraction procedure and in their extent of ionization, thus resulting in greater accuracy and precision.

For air the target PFOS related analytes are the perfluorosulfamido alcohols, acrylates and PFOSA (van Leeuwen and de Boer 2007; Jahnke *et al.* (2007). These compounds are neutral and semi-volatile and thus more similar to conventional POPs. Most studies extracted them by passing air through a cartridge containing XAD resin sandwiched between polyurethane (PUF) plugs. PFOS and related anionic PFCs, as well as the perfluorosulfamido alcohols may also be on air particles and can be determined by analyzing a filter placed in front of the PUF-XAD sandwich. These neutral PFCs are eluted from the PUF/XAD by a combination of medium polar organic solvents such as methanol, petroleum ether and ethyl acetate (van Leeuwen and de Boer 2007). The filter can be analysed for PFOS following methods used for other solid samples *e.g.* by extraction with methanol (Shoeib *et al.* 2005).

5.3 POPs analysis

Since the 1960s, lipophilic POPs (typically chlorinated and more recently also polybrominated substances) have been determined using gas chromatography (GC) techniques with electron capture detection (ECD), initially using packed columns. Today the separation has been improved by the use of capillary columns and the selectivity by the use of mass spectrometric detectors (MS). These techniques can also be applied to the volatile perfluorosulfamido compounds which are included in the list of PFOS related compounds in Annex B of the Stockholm Convention. However, the analysis of PFOS and related anionic PFCs these compounds typically requires the use of liquid chromatographic separation and mass selective identification and quantification (LC/MS). Therefore, a general differentiation between GC and LC methods needs to be made; although the same QA/QC criteria have to be applied to both techniques.

Based on the availability of commonly used instruments for the determination of POPs, three types of laboratories for the lipophilic, semi-volatile POPs (1, 2a, 3) and one type of laboratory (2b) for PFOS and anionic PFCs can be identified, as described in Table 5.1.

Table 5.1: Requirements for the instrumental analysis of POPs including PFOS related compounds.

Laboratory instrumentation level	Equipment	Infrastructure needs	Chemicals
5	Sample extraction and clean-up systems (manually or automated), LC-MS/MS)	Nitrogen/air conditioning/consistent power/high operational costs/personnel specifically trained to operate and troubleshoot complicated instrumentation	PFOS and other anionic PFCs , PFOSA
3	Basic sample extraction and clean-up equipment, capillary GC-ECD	Nitrogen/air conditioning/power/ personnel specifically trained to operate and troubleshoot equipment problems	PBB, most PCB and all OCPs except toxaphene
2a	Sample extraction and clean-up equipment, capillary GC-LRMS – electron ionization mode	Helium/air conditioning/ consistent power/ personnel specifically trained to operate and trouble-shoot equipment problems	PBB, most PCB and all OCPs; Also perfluoro-sulfamido alcohols in positive chemical ionization mode
2b	Sample extraction and clean-up equipment, capillary GC-LRMS – negative chemical ionization mode	Methane or other moderating gas/air conditioning/ consistent power/ personnel specifically trained to operate and trouble-shoot equipment problems	PBDE and PBB, as well as toxaphene and other highly chlorinated (≥ 4 Cl) OCPs
1	Sample extraction and clean-up equipment, capillary GC-HRMS	Helium/air conditioning/ consistent power/high operational costs /personnel specifically trained to operate and troubleshoot complicated instrumentation	PCDD/PCDF, all PCB, all OCPs, PBB, all PBDE

GC-ECD – gas chromatography/electron capture detection

GC-LRMS – gas chromatography/low resolution mass spectrometry

GC-HRMS – gas chromatography/high resolution mass spectrometry

LC-MS/MS – high performance liquid chromatography/tandem mass spectrometry

PY – Person-year

Although it is very difficult to estimate operational costs according to instrumentation level, the table below is providing some orientation on investment costs as well as on consumables according to best knowledge of the experts and assuming operation of an average routine laboratory:

		USD
Instrumentation - Analytical laboratory		
GC-ECD with autosampler	Investment	40,000
GC-LRMS with autosampler	Investment	140,000
GC-HRMS with autosampler	Investment	700,000
LC-MS/MS with autosampler	Investment	200,000
Air samplers		
		USD
Low-volume sampler	per piece	10,000
Passive air sampler	per piece	150
Consumables		
Quartz filter plus PUF plugs	per set	
Pre-cleaned PUF plugs/disks	per disk	20
Analysis to third parties (cost per sample)		
	Preferred method	USD
PCDD/PCDF	HRGC-HRMS	900
dl-PCB (when in addition to PCDD/Fs)	HRGC-HRMS	350
TEQ (total)	HRGC-HRMS	1,150
POPs pesticides+indicator PCB	HRGC-HRMS, HRGC-LRMS, HRGC-ECD	550
PBDE	HRGC-LRMS	300
HBCD	HRGC-LRMS	100
HBCD isomers (LC)	LC-MS/MS	200
PFOS	LC-MS/MS	220
Materials and consumables		
		USD
HRGC columns (60 m)	per piece	880
Native pesticides standard mix	per unit	200
Labelled LRMS pesticides standard mix (calibration, clean-up, syringe)	per set	5,200
Labelled indicator PCB standard mix (calibration, clean-up, syringe)	per set	1,500
Labelled LRMS PCDD/PCDF standard mix (EPA 8280, calibration, clean-up, syringe)	per set	4,200
Labelled HRMS PCDD/PCDF standard mix (EPA 1613, calibration, clean-up, syringe)	per set	2,820
Labelled HRMS dl-PCB standard mix (WHO-TEF mix, calibration, clean-up, syringe)	per set	2,100
Labelled MS PBDE standard mix (calibration, clean-up, syringe)	per set	
Labelled MS PFOS standard mix (calibration, clean-up, syringe)	per set	

More detailed information can be taken from the UNEP POPs Laboratory Databank where many laboratories have provided costing information for analysis to third parties.

During the period of the first phase of Global Monitoring Plan leading to the first regional and global reports, recommended methods and instrumentation as shown above have been applied and shown useful. It is anticipated that in the same way, the analytical methods will be developed and agreed for the newly listed nine POPs. Further, improved methods as they may appear over the life of the Global Monitoring Plan can be included into the guidance document and adopted.

Quality control and quality assurance are important factors in sampling and analysis. As a general rule, it is recommended to spend about 20% of all efforts for QA/QC.

Whereas the Global Monitoring Plan does not prescribe any specific method for the analysis of POPs takes a performance-based approach, any method performance must be verified through control tables where optimal operational ranges are defined, and the periodical analysis of certified reference materials, own laboratory reference materials, and blind or divided samples. These steps should be included in routine QA/QC. The inter-calibration exercises are an essential component in quality assurance for the laboratories to improve or maintain quality of results and to generate trust in the results. A recommendation would be that at least once a year such an intercalibration study is performed for each relevant matrix and group of persistent organic pollutant of interest to the Region.

Numerous analytical approaches are available for quantifying PCB, and OCPs, as well as PCDD/PCDF by gas chromatography. As with extraction/separation steps only general guidance is required for *ortho*-substituted PCB and OCPs. Some general guidance on the application of gas chromatographic analysis of *ortho*-substituted PCB and OCPs is provided in Table 5.2. For PCDD/PCDF and dioxin-like PCB, quantification solely by isotope dilution HRMS is recommended and details can be found in standard operation procedures (SOPs) (e.g., EPA method 8290A, EPA methods 1613 and 1668).

Obviously, HRMS can also be used for the determination of all PCB, including congener-specific determination of non-*ortho* and *mono-ortho* substituted PCB (e.g., EPA method 1668) as well as OCPs and indeed would provide a very high level of confidence in the results compared to GC-ECD. However, use of GC-ECD is recommended for indicator PCBs because of its wide availability, relatively low cost, and the substantial knowledge base that exists on the use of this technology for analysis of *di-ortho* PCB at low ng/g levels or higher in environmental matrices. OCPs are often analysed by GC-ECD but can be done with much better accuracy by GC/MS and use of labeled standards. Another recent development is that of Time-of-Flight MS instruments (ToF-MS). These bench-top MS instruments nowadays offer resolution that even exceeds that of the traditional HRMS instruments. It is expected that in the near future these instruments will replace the traditional HRMS sector instruments, also for the analysis of PCDD/Fs and non-*ortho* PCBs.

The following information has been compiled to guide laboratories and sampling team engaged in POPs analysis on the sensitivity of the analytical methods as well as on the amount of sample needed.

For water as a matrix the following orientation could be helpful:

	Unit	HRMS	LRMS	ECD
PCDD/PCDF				
dl-PCB				
TEQ (total)				
POPs pesticides/HCH	pg L ⁻¹	1	1	1
indicator PCB				
PBDE				
PFOS	pg L ⁻¹		5-10	

The red field indicates that this instrumentation in combination with the respective matrix is not recommended for the GMP.

Substance group/ Matrix-instrumentation	Mothers' milk/ Human blood				Ambient air				Instrumentation/method detection limit				Ionization mode
	Unit	HRMS	LRMS	ECD	Unit	HRMS	LRMS	ECD	Unit	HRMS	LRMS	ECD	
PCDD/PCDF	pg TEQ g ⁻¹ fat	1			pg PUF ⁻¹ or fg m ⁻³				pg □L ⁻¹	0.05			
dl-PCB	pg TEQ g ⁻¹ fat	1			pg PUF ⁻¹ or fg m ⁻³				pg □L ⁻¹	0.1			
TEQ (total)	pg TEQ g ⁻¹ fat	1			pg PUF ⁻¹ or fg m ⁻³				pg □L ⁻¹	0.1			
OC Pesticides (<6 Cl)	ng g ⁻¹ fat				pg PUF ⁻¹ or fg m ⁻³		1-5		pg □L ⁻¹	0.5	0.5	0.5	EI-MS
OC Pesticides (>=6 Cl)	ng g ⁻¹ fat				pg PUF ⁻¹ or fg m ⁻³				pg □L ⁻¹		0.1	0.1	ECNI-MS ¹
indicator PCB	ng g ⁻¹ fat				pg PUF ⁻¹ or fg m ⁻³		1-5		pg □L ⁻¹	0.5	0.5	0.5	EI-MS
PBDE	ng g ⁻¹ fat				pg PUF ⁻¹ or fg m ⁻³		1-5		pg □L ⁻¹	0.5	0.1		ECNI-MS
HBCD	ng g ⁻¹ fat				pg PUF ⁻¹ or fg m ⁻³				pg □L ⁻¹	0.5	0.1		ECNI-MS
HBCD (LC)	ng g ⁻¹ fat				pg PUF ⁻¹ or fg m ⁻³				pg □L ⁻¹		0.5		LC-MS/MS APCI ²
PFOS	pg mL ⁻¹				pg PUF ⁻¹ or fg m ⁻³				pg □L ⁻¹		1		LC-MS/MS negative ESI

Notes:

The red field indicates that this instrumentation in combination with the respective matrix is not recommended for the GMP

1: Electron capture negative ion MS is the preferred mode for PBDE and also for highly chlorinated OCs including endosulfan, chlordane, toxaphene

2: HBCD isomers are also analysed by LC-MS/MS in positive chemical ionization mode; or as with PBDE by GC-MS with ECNIMS

5.4 Data treatment

There are a number of parameters that have to be reported together with the analytical results. These include the efficiency of the extraction and clean-up, and the blank values, but the results should not be compensated for these parameters. The uncertainty of the results should also be at least estimated, but preferably determined, using results from inter- or intralaboratory comparisons.

The lowest concentration at which a compound can be detected (limit of detection, LOD) is defined as that corresponding to a signal equal to three times the noise. The lowest concentration that can quantitatively be determined (limit of quantification LOQ) is 3.3-fold higher than the LOD. Compounds found at levels between LOD and LOQ can be reported as present, or possibly as being present at an estimated concentration, but in the latter case the result has to be clearly marked as being below LOQ. Results below the detection limit should be reported as <"LOD" with a realistic figure for the LOD.

There are, however, several statistical techniques for treating censored data when the true detection limit is known, *e.g.* by using a robust statistic such as the median which is unaffected by small numbers reported as below LOD.



Figure 5.2: Example of substitution of concentrations reported as less than LOD, by extrapolation from regression of concentrations from the same annual sample above LOD on rank order. Log-linear regression fitted to data above LOD. Dots = concentrations above LOD, Triangles = substituted values for concentrations reported as below LOD, Squares = LOD/2 – values.

Another method uses an estimate of each unknown concentration based on the empirical expected order statistic (Helsel and Hirsch, 1995). This method fits a log-linear regression of the ranked detected concentrations on rank, and then uses this relationship to predict the value of those concentrations reported as below the limit of detection (Figure 5.2).

Results may also be reported as being in the interval between a value where the lower limit is based on non-quantifiable peaks set to zero and an upper limit where results below LOQ are set as equal to the LOQ.

In the analysis of complex mixtures, such as PCB, there is always a risk for co-eluting peaks in the gas chromatograms, and known interferences should be reported.

5.5 Organization of quality control

Quality assurance (QA) in all steps from sampling, through analysis and data reporting is essential to allowing comparison of data from multiple sources, both between and within regions.

Data with inadequate quality represent at best a waste of resources, and at worst have the potential to undermine the results of the effectiveness evaluation.

Requirements for the level of data comparability can vary. For example, geographical or spatial trends require an adequate degree of comparability across the geographical area concerned. However, data from a particular source that are 'incomparable' in a geographical context may still be suitable for determining temporal trends as long as their 'bias' is consistent over time.

For those components of quality assurance that relate to laboratory analysis of samples, it is essential that all laboratories that are involved in generating data for the GMP operate an appropriate 'in-house' QA/QC regime. This should include, for example, maintenance of control charts based on the regular analysis of internal reference materials, and periodic analysis of appropriate certified reference materials, where these are available. Making available reference materials to laboratories that do not have access to them may be one important component of building analytical capacity.

A further component of the QA regime practised by most with good QA practises is regular and routine participation in national, regional or global intercomparisons (intercalibration exercises, ring-tests, laboratory performance testing schemes, etc.). Some coordinated monitoring programmes require participation in such exercises. International intercomparisons represent a useful means of evaluating comparability between participating laboratories, but will always reflect their performance 'on the day'. Laboratory performance testing schemes are typically designed to provide a more continuous evaluation of laboratory capability.

The organization of quality assurance/quality control (QA/QC) warrants special attention under the GMP. Recommendations pertaining to QA/QC are found in various sections of this document. To be able to ensure that data generated by the GMP are of adequate quality, there will be a need for overarching activities such as:

- Distribution of appropriate analytical standards and reference materials;
- (Requiring) participation of laboratories in relevant (*e.g.* internationally recognized) intercalibration and laboratory performance testing schemes;
- Where necessary, organization of new intercalibrations or laboratory performance testing schemes;
- Where necessary, production of (new/necessary) reference materials.

5.6 References

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Examples: Analytical Methods for POPs Pesticides

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EPA Method 8081A: Organochlorine Pesticides by Gas Chromatography (and ECD)

ISO 6468 (1996) Water quality – Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes – Gas chromatographic method after liquid-liquid extraction

ISO 10382 (2002): Soil quality – Determination of organochlorine pesticides and polychlorinated biphenyls – Gas-chromatographic method with electron capture detection

EPA Method 8081A: Organochlorine Pesticides by Gas Chromatography (and ECD)

Examples: Analytical Methods for PCB

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EN 12766-1 (2000): Petroleum products and used oils – Determination of PCBs and related products – Part 1: Separation and determination of selected PCB congeners by gas chromatography (GC) using an electron capture detector (ECD)

EN 12766-2 (2001): Petroleum products and used oils – Determination of PCBs and related products – Part 2: Calculation of polychlorinated biphenyl (PCB) content

EN 61619 (2004): Insulating liquids – Contamination by polychlorinated biphenyls (PCBs) – Method of determination by capillary column gas chromatography

EPA Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS, United States Office of Water, EPA No. EPA 821-R-00-002, Environmental Protection Agency (4303), December 1999

EPA Method 8080: Organochlorine Pesticides and PCBs

EPA Method 8082: Polychlorinated biphenyls (PCBs) by gas chromatography (www.epa.gov/epaoswer/hazwaste/test/pdfs/8082.pdf)

EPA Method 8275A: Semivolatile organic compounds (PAHs and PCBs) in soils/sludges and solid wastes using thermal extraction/gas chromatography/mass spectrometry (TE/GC/MS), EPA analytical chemistry guidance SW-846

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ISO 10382 (2002): Soil quality – Determination of organochlorine pesticides and polychlorinated biphenyls – Gas-chromatographic method with electron capture detection

JIS K 0093 (2002): Testing method for polychlorobiphenyl in industrial water and wastewater

Examples: Analytical Methods for PCDD/PCDF and dl-PCB [FORMAT: move to next page?]

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- EPA Method 8290A: Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS), revision 1 January 1998
- EPA Method T09: Determination of polychlorinated dibenzo-p-dioxins (PCDDs) in ambient air using high-resolution mass spectrometry (HRGC/HRMS)
- EPA Method 8280A: The analysis of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans by high resolution gas chromatography/low resolution mass spectrometry (HRGC/LRMS) (EPA analytical chemistry guidance SW-846)
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- STAP/GEF workshop report <http://www.unep.org/stapgef/documents/popsJapan2003.htm>

WHO GEMS/Food <http://www.who.int/foodsafety/chem/gems/en/>

UNEP Regional Seas Program <http://www.unep.org/water/regseas/regseas.htm>

National monitoring activities http://www.chem.unep.ch/gmn/02_natpro.htm.

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Japan Environment Agency <http://www.env.go.jp/en/topic/pops/index.html>

ICES <http://www.ices.dk/env>

OSPAR <http://www.ospar.org>

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6 DATA HANDLING

6.1 Objectives and priorities

The results from the Global Monitoring Plan will be used to determine trends from monitoring of POPs globally to support the effectiveness evaluation of the Stockholm Convention. A primary goal is therefore to obtain (comparable) data that are capable of revealing trends over time in emissions and/or exposure to contaminants of concern, in the various regions.

Effective sharing and delivery of necessary data and information by contracting parties is essential to achieving this objective. The data provided need to:

- Be relevant, to the objectives of the effectiveness evaluation of the Stockholm Convention;
- Have sufficient quality and level of detail;
- Be consistent and comparable over time;
- Be transparent, and to the greatest possible degree public and unrestricted.

6.2 Data policy

6.2.1 Terminology

To avoid confusion, it is important that some basic terms and concepts that are used in this document are defined so that they are understood to mean the same thing by all parties:

- **Primary GMP data:** are the results of measurements made on samples collected under the auspices of the GMP, or other programmes that are compatible with the goals of the GMP. They include both measurements of POPs in specific samples, and measurements of other covariables relating to these samples (*e.g.* biological covariates), that are necessary to interpret the POPs data in a meaningful way, including the location and timing of sampling.
- **GMP meta-data:** are any other data or information that describe the *primary GMP data* in some way. This can include information on the methodologies employed (*e.g.*, for sampling and analysis) and the laboratories responsible for a particular set of analyses, or the design and implementation of programmes that contribute to the GMP, etc.
- **Supplementary data:** Are any other data or information that may be accepted for use in the Stockholm Convention evaluation process. This might include relevant information and/or data from published sources (*e.g.* the peer reviewed scientific literature, existing assessment, etc.), results of modelling activities that may assist the data interpretation and evaluation, or results of research activities that may be relevant to interpreting the *primary GMP data* in a valid and meaningful way (*e.g.* process studies, food-web studies, etc.). Such data will comprise an important contribution to the Stockholm Convention evaluation process, especially in the initial period where the necessary data management infrastructure is still under development in some regions.

Primary GMP data (and supplementary data where these concern monitoring results from *e.g.* published sources) can be further sub-divided between:

- **Un-aggregated data:** individual sample measurement values (*e.g.* the concentration of PCB153 in the liver tissue of a specific individual fish, sampled at location x at time y).
- **Aggregated data:** (statistically) summarised data, *e.g.* averaged values that summarise the measurements on a number of individual samples.

6.2.2 Data policy

The GMP data handling activities should promote transparency of process, both with respect to the data themselves, and how they are treated and analysed. The GMP data policy should also have the goal of ensuring access (for the purposes of the Stockholm Convention evaluations) to the most relevant and up-to-date information available. Some countries may request that GMP data for their country should be endorsed.

In considering potential public access to data, a distinction is usually made between un-aggregated data, aggregated data, and high level meta-data. Sensitivity with regard to making data publicly available generally decreases in the order un-aggregated data > aggregated data > high level meta-data; with high-level meta-data normally not subject to any restrictions.

Part of the data generated under the GMP will already be in the public domain, being made available for public access soon after their generation. Other data, however, may be restricted; for example, subject to a moratorium to allow scientists responsible for the data to publish their results before the data are made public.

Use of data for the purposes of the Stockholm Convention evaluations should not compromise the rights of the data owners. Data owners should therefore be fully informed of how their data will be used, and what parts of the data or results will be made public and when in order to ensure that they are in agreement. Furthermore, full and appropriate acknowledgement of data sources should be a key part of the data policy.

To facilitate the above, for all data delivered from the GMP:

- The data owners should be identified (note: this is not always the same as the data provider);
- Any conditions relating to restrictions to making the data publicly accessible should be properly described (by the data owners);
- The required citation/acknowledgement to the data should be provided (by the data owners).

6.3 Data to be reported

Minimum data reporting requirements are necessary to ensure consistency both within datasets over time and among the datasets between regions.

Ideally, un-aggregated data (individual sample measurement values) should be reported. Where data are reported as statistically aggregated data (averages):

- The type of statistical average concerned (*e.g.* average, geometric mean, median) should be clearly indicated; and
- The data should also include an estimate of variability (standard deviation, standard error, confidence interval, etc.).

Air (monitored at sites unaffected by local contamination) and human tissues (breast milk or blood) have been identified as the core monitoring matrices under the GMP. However, the data handling routines should also accommodate results from monitoring of other types of environmental sample identified under the GMP (bivalves, tissues and organs of other biota, etc.). Where data on core or additional identifies GMP matrices are not available, some flexibility will be retained to allow use of other relevant data, for example POPs levels in food, etc.

6.3.1 Contaminants data

Contaminants of concern are those that are identified under the Stockholm Convention GMP (see Chapter 2). To the greatest extent possible, data should be reported for individual compounds or congeners or isomers.

Data on contaminant concentrations should be reported together with a clear indication of both the units and the basis of determination (wet weight, lipid weight, etc.). Recommended units and basis of determination for GMP priority matrices are as follows:

	Air	Human milk and blood	Tissues and organs of other biota
All POPs except PCDD/PCDF	pg/m ³	ng/g lipid	ng/g lipid
PCDD/PCDF	fg/m ³	pg/g lipid	pg/g lipid

pg/g = pico-grams per gram = 10^{-12} = nano-g/kg

fg/g = femto-grams per gram = 10^{-15} = pico-g/kg

6.3.2 Co-factors and methodological information

In addition to reporting of data on contaminant concentrations in the various media, the goals of the GMP require that sufficient supplementary data and information are also reported to allow valid interpretation of, for example, time-series datasets. This includes, for any individual dataset, reporting:

- The sampling location(s) concerned (including site description);
- The time of sampling (or the time period represented by the dataset);
- Data on other factors that may be relevant to interpretation of temporal trends (for example, age/size of animals sampled, volumes of air sampled, information on smoking or dietary habits of the sampled populations, methods employed, etc.);
- Data on parameters to allow conversion between reporting basis (e.g. % lipid and methods used for lipid determination);
- Information on methodologies employed for sampling and analysis, QA/QC routines;
- Information on results of laboratory performance in (international) intercalibration exercises and laboratory performance testing schemes.

Further details of the reporting requirements will need to be determined when the particular regional monitoring plans will be specified in greater detail.

6.3.3 Limit of detection, limit of quantification

Definitions of the limit of detection (LOD) and the limit of quantification (LOQ) are defined in Chapter 5.4 of this document.

Non-detects should normally be reported as 'less than the LOD', the value of which has to be reported; *i.e.* if the limit of detection is 0.5 ng/g lipid, a non-detect should be reported as <0.5 ng/g lipid.

6.3.4 Derived parameters

Derived quantities, such as normalized or adjusted values or parameters such as TEQs or sums of congeners should normally be produced by those responsible for evaluating the data, on the basis of the reported data for individual congeners, etc.

If it is agreed that derived values may be reported; then a detailed definition of the methodology to be applied should be provided, including description of how to incorporate values below the detection limit, TEF to be applied, etc.

For TEQ calculation in the case of PCDD/PCDF analysis, it is strongly advised that upper bound and lower bound values be reported in keeping with the recommendations by JECFA (Joint FAO/WHO Expert Committee on Food Additives).

6.4 Data quality

Prior to being accepted for use in the Stockholm Convention process, it is recommended that data should be accepted, through an independent evaluation, as having ‘appropriate quality’.

Data quality requirements shall be the same for all regions; where necessary, the objective will be to build capacity, not to reduce requirements to the lowest common denominator.

Data quality evaluation involves several components at different stages:

- Data should be evaluated at source as being of appropriate quality before they are reported. This includes application of appropriate methodologies and QA/QC routines during sampling and within the laboratory. Data should be scrutinized by the laboratory generating them and thereafter by a coordinator of the programme from which the data are sourced, who among other things should check that the data have been correctly transcribed and compiled and are complete with respect to the reporting requirements. The data provider should ensure that this has been done before data are reported.
- Upon reporting, where the possibility exists, data should be subject to data quality checking at, for example, data centres – where routines should be available for checking completeness of data submissions and may be available for conducting basic checks including inter-component comparisons (*e.g.* relative concentrations of different parameters/congeners) and cross-comparisons of data from different sources. Data centres should provide data quality feedback to data sources.
- Finally, the data, confidence intervals and all supporting information on QA, sampling and analytical methods, etc. should be evaluated by a regional data quality review panel¹⁰ responsible for accepting the data for use in the Stockholm Convention effectiveness evaluations.
- A system may need to be developed for flagging data that, *e.g.*, lack appropriate QA/QC information, do not fulfil all quality criteria, or are between the LOD and the LOQ, but which may still be acceptable for some purposes in the Stockholm Convention evaluation process.

In addition to QA/QC considerations relating to the accuracy of the results themselves, QA/QC routines need to be implemented to ensure that quality is maintained during the data exchange process. Data compilation and data reporting include a number of steps where (considerable) potential exists for introducing errors: data entry, application of algorithms used in data conversion or transformation, data communication, etc. This is especially so when data are transferred beyond the ‘horizon’ of those, who are most familiar with them and therefore best placed to spot apparent discrepancies, *i.e.* those responsible for collecting/generating the data. It is therefore recommended that:

- An appropriate chain of custody is established from the data originator to the data quality review panel. This chain should be as short as possible.
- At each point of transfer in the chain, those responsible for delivering and receiving the data should sign-off to confirm that the data have been correctly and accurately transferred. In practise, this involves (a) data recipients confirming that data delivered to them meet the necessary requirements and specifications for delivery, (b) data recipients preparing summary data products (maps, summary statistics, etc.) that will allow data errors or discrepancies introduced during the transfer to be detected, which are returned to the data deliverer (c) the data deliverer examining these products and confirming that the data appear to be correctly transferred. Ultimately, any GMP data evaluations/products should be returned to the data sources for their comment/confirmation.

¹⁰ Data quality review and assessment panels may be identified within the regional organization groups (see Chapter 7 for details)

6.5 Data flow and storage facilities

6.5.1 Scope

The main goal of the Global Monitoring Plan data strategy is to compile un-aggregated - primary GMP data. Un-aggregated data permit data to be treated in a transparent and consistent manner according to agreed assessment methodologies. If these methodologies are modified or further developed at some point in the future, the availability of un-aggregated - primary GMP data provides the best possibilities for re-calculation or for repeating previous data treatment. Aggregated data provide much more limited potential for re-analysis or for combining data from different sources. Most data derived from supplementary information will be aggregated (unless they are otherwise accessible as un-aggregated data from data centres/archives).

That part of the GMP meta- data that detail methodologies employed in the collection and generation of the primary GMP data, as well as laboratory intercalibration/testing scheme results should follow the primary GMP data and also be reported to data centres, as well as being made available in an appropriate form to data assessment groups. Since intercalibration / performance testing results available from the organizers of these exercises are often referred to an (undisclosed) laboratory code system, these results will need to be reported by the laboratories themselves, along with the measurement data.

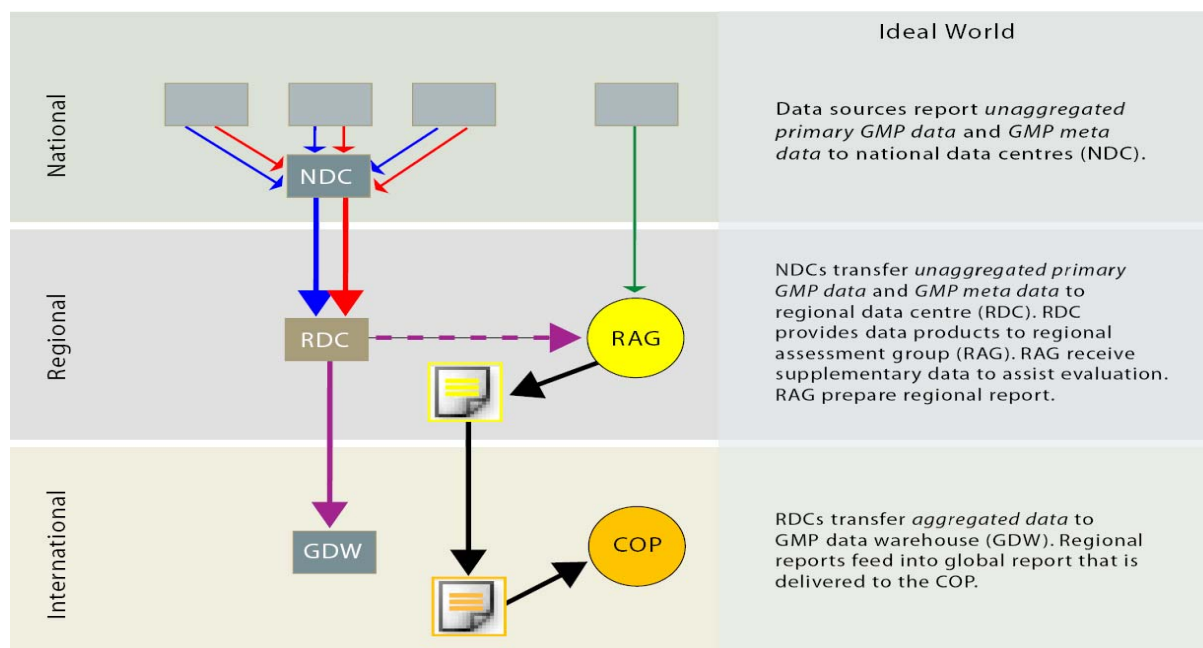
The data flow for the GMP outlined here focuses on reporting and compilation of data at the international level. Organization of data compilation and reporting at the national level is assumed to be the responsibility of the participating countries. However, participating countries, Parties to the Convention, requiring assistance to build capacity in this respect may look to the GMP for such assistance, including exchange of experience between Parties and countries.

6.5.2 GMP data storage (compilation and archiving)

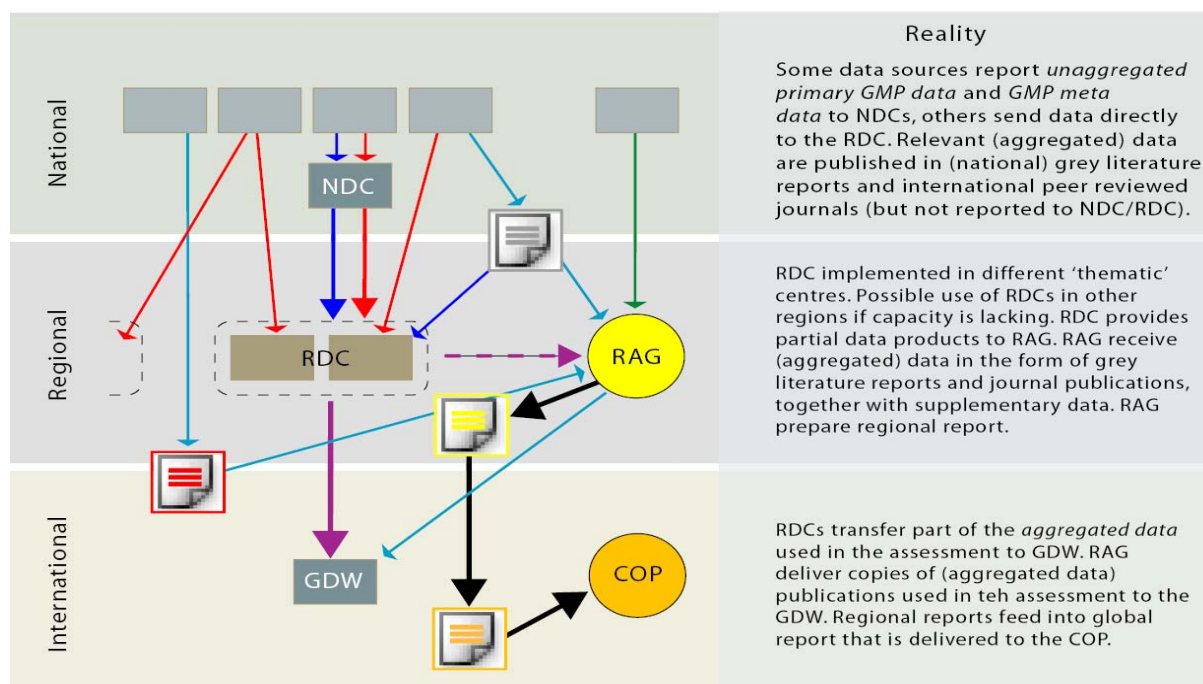
The data reporting model that is being suggested involves compiling and archiving primary GMP data within a 'regional data repository' in each of the 6 geographic regions.

In addition to the regional data centres, a single GMP 'data warehouse' will be established to compile and archive aggregated data, data products and results, including supplementary data that are used in the Stockholm Convention evaluations. A primary purpose of the GMP data warehouse will be to provide transparency to the process, facilitating access to the data and results that are the basis for any conclusions of the (sufficiency and effectiveness of the) evaluations. The GMP data warehouse could also function as the data centre for maintaining the database of meta-data, including meta-data on GMP implementation in the various regions, and information and documentation that may be required by assessment groups concerned with, for example, data quality evaluations, such as information on laboratory performance.

This ideal solution for a particular region is shown in the following flow-chart (1).



In reality, however, this ideal solution is unlikely to be achieved. The following flow-chart (2) below shows the more likely situation, at least for some regions for some time to come.



Due to the desirability of ensuring that data are handled in centres with appropriate expertise to understand the data concerned, it may well be appropriate, also in regions with well-developed existing data centres, that rather than a single physical location, the regional data repository is implemented through a limited number of specialist thematic centres; as few as necessary to cover the type of data involved, with preference being given to centres that are capable of serving as regional centres for multi-disciplinary datasets (blood/milk, etc.).

If appropriate data centres cannot be identified in one or more regions, a temporary solution should be identified to facilitate data handling while the necessary capability is being established within the region; one possible option being to use facilities that may exist in neighbouring regions.

Capacity building for GMP data management activities will be essential in several regions. One way to efficiently implement this would be to establish model solutions in some regions and then consider possibilities for technology transfer (*e.g.* these model centres make their existing database developments available to other centres – under some suitable licensing agreements to avoid infringing intellectual property rights) and staff training to implement data centres in other regions. Effort will also need to be expended to support data management capability at the data sources, both to educate data sources in the needs and requirements of the GMP and to realise the data delivery; this also is not just a problem for developing areas but also a major obstacle to data flow in areas with existing programmes and data flow. It is critical that data reporting is an integral part of GMP (monitoring) implementation at every level – from simple pilot projects to national activities in the most advanced countries – data management should not be an ‘add-on’ exercise. It should be recognized that data-management may consume up to 5-10% of a monitoring programme finances; however, without this investment the other 90% of the expenditure is largely wasted.

6.5.3 Selection of GMP data centres

Selection of GMP data centres should take account of the following:

- Data should be compiled in centres that are founded on a basis that will secure their continuing existence and stability over a long-period of time (decades at least); centres lacking a secure long-term funding perspective should be discounted.
- Data should be compiled at centres where the in-house staff possesses the appropriate expertise, both in terms of data management and understanding of the types of data being handled.
- Data should be compiled at centres possessing the necessary technical resources and equipment for the required data handling, including communications and transfer of data, secure data storage (including on-site and off-site back-up), preparation of data products, etc.

The GMP is envisaged as a long-term activity. In some cases several years of data will be required before reliable interpretation of trends can be achieved. Disruption to the data management process through frequent changes in the (location of or operations at) data storage facilities should be avoided.

A number of data centres or programmes exist today that could be considered either as candidate GMP data storage facilities within a region, or as centres that could partner or facilitate capacity-building of storage facilities in other regions. Some of these are presented in Table 6.1.

6.5.4 Standardized data exchange and reporting systems

Reporting of data in a manner that is technically feasible and reasonably convenient for all parties concerned, minimizes the potential for errors and ensures that all reporting requirements are met is a major challenge.

GMP data exchange will probably involve use of a wide variety of formats. Data reporting systems should therefore aim to be as flexible as possible, while at the same time trying to promote the maximum possible degree of standardization. Some constraints will need to be imposed to ensure that data reported meet the minimum requirement with regard to content and level of detail.

Compilation of data according to agreed standards is also important if they are to be used in connection with modelling activities, for example for the understanding of environmental transports within and between regions. If properly implemented, the GMP data warehouse will constitute a potential source of data that can be used for model validation, etc. However, this subject is not addressed further in this guidance document.

Definition of a standardized format for use in data exchanges between the regional storage facilities and the GMP data warehouse will probably be necessary in order that the data warehouse can serve its intended purpose.

The problems and costs involved in developing new data exchange systems, and reporting formats databases, and in adapting databases to accommodate new systems should not be underestimated. Maintaining existing databases is, in itself, a costly matter that may well require additional resources if

centres are requested to handle larger volumes of data. All efforts should therefore be made to make the best possible use of existing developments/centres, and to avoid 're-creating the wheel'. Collaborating in data handling efforts with established programmes and 'buying' data handling services from existing operations will likely be more cost effective than setting up new systems from scratch in many regions, and avoid duplication, and the possible negative consequences for all parties associated with this. At the same time, the diversity in regional capabilities in this connection needs to be recognized. In some regions, new data handling capability may need to be developed. Here again, cooperation (*e.g.* partnerships) with existing well-functioning systems in other regions may well have advantages, both financial and in terms of time required to implement capacity.

6.5.5 Some complicating factors

There are a number of issues that need to be addressed, both in relation to data management and in a wider context within the GMP. Not the least of these is language. It may or may not be practical to insist on use of a common language (*e.g.* English, or the most widely used language within a region). However, at a certain point in the path from data source to data warehouse, language barriers will need to be bridged. Data reporting is not a one-way process. Those responsible for compiling and archiving data, or for evaluating and assessing data will want to address questions back to data sources, requests for missing components, requests for clarification, etc. This also applies to technical aspects of data, for example PCB to one person may mean polychlorinated biphenyl and to another pentachlorobenzene, agreement on and adoption of standardised coding for use in data reporting should be a matter of priority.

Relevant data are potentially available from many sources, both official (governmental) and other (*e.g.* universities, peer reviewed literature). The Stockholm Convention evaluations will presumably need to make use of data from several sources, not all of which will be available in the form of data files. The GMP data warehouse at least will need to be able to accommodate data in several formats, including documentation in electronic or hard-copy formats.

In addition to restrictions on data that may be imposed by the data owners for proprietary reasons, some types of information are sensitive and subject to national legislation concerning data confidentiality. Data on humans is a case in point. Data restrictions will typically apply that prevent any data being identified with a particular individual – and therefore data that are made available for international exchange tend to have a high level of aggregation, which can conflict with the desire for detailed information. Conversely, some countries have legislation that requires that data are made public. Both of these situations need to be taken into account in developing the GMP data strategy.

6.6 Data analysis

To promote comparability among the regions, harmonized assessment tools (such as statistical methods for temporal trend evaluations) and products should be agreed. This again will need to be determined in association with the further elaboration of the monitoring plan and the associated assessment methodology. Some international programmes (*e.g.*, OSPAR, AMAP, EMEP) are already employing standardized methods that could be considered for adoption by the GMP.

The reliable identification of trends will require that statistical evaluation be carried out on the design of each national trend monitoring programme contributing to the GMP, to ensure that it is powerful enough to detect trends of interest. This will involve establishing the target accuracy of the analysis.

It should be kept in mind that the statistical power is likely to be reduced when data from several laboratories are combined. Given the expected variability, based on results of inter-laboratory studies, it is recommended to record site-specific trends in POPs concentrations based on results of single laboratories.

6.7 Cost and financial implications

The costs of establishing the necessary systems within individual countries to allow them to collect and report data to GMP regional data centres are almost impossible to estimate. They will depend on both the volumes of data involved and the existing capacity within the country concerned. The governmental structures and way in which relevant institutions are organized and funded are additional factors. These will vary widely from country to country. Where capacity is lacking, capacity building mechanisms should be applied to institute the required infrastructures.

With regard to operation of GMP regional data centres, this will similarly differ from region to region depending on the existing situation, and in particular the availability of existing data centres that could serve as the regional centre (or a thematic component within a regional centre network). However, at this level the costs of operating the regional data centre(s) should be possible to estimate based on similar activities within other programmes. Costs essentially comprise two components:

- **Establishment costs:** the initial investments necessary to equip a data centre with the necessary technology, and to implement (develop or adapt) databases and data handling routines so that they meet the requirements of the GMP.
- **Operating costs:** the costs to handle the GMP data on a routine basis, to receive data, apply QA/QC procedures, archive data in databanks, and produce required data products (in support of assessment activities). These are recurring costs, and primarily concern staff employment to handle the GMP datasets. These costs are partly a function of the volume (and complexity) of data involved.

Use of existing data centres can significantly reduce (or entirely eliminate) the need for establishment costs. Operating costs can also be substantially reduced by utilising data centres that are also used by other (international) programmes, thus avoiding the need to duplicate reporting of data that may serve several purposes/programmes; this also reduces the burden on the countries involved. Similarly, harmonization in data management procedures, data analyses and data products can all lead to cost-effective data handling solutions.

In some regions it may be possible to implement operation of regional data centres on the basis of cost sharing agreement between the countries in the region; in other cases, and also probably for the GMP 'data warehouse', this may need to be identified as a core activity requiring some central funding.

Several international programmes (AMAP, OSPAR, etc.) and their respective data centres (see Table 6.1) should be able to furnish relevant information on financing of data activities that can be used as a basis for estimating costs of establishing and operating data (regional) centres.

Not included in the above, are the additional costs of data assessment activities; for example convening expert groups to conduct evaluation and assessment of GMP data.

6.8 Acceptance of data and information for inclusion in the evaluation

The effectiveness evaluation shall take account of data and information from a range of sources, as long as these are deemed to be of appropriate quality and are considered relevant to the objectives of the effectiveness and sufficiency evaluation.

In practise, most of the data compiled under the GMP are likely to arise from governmental monitoring activities, agencies and institutes. However, and especially until such time as capacity is fully established in all regions, the evaluation should also include data and information from other relevant sources, such as the peer reviewed scientific literature or data compiled under international programmes.

At an early stage in the implementation process, the GMP regional organization groups (ROGs) should compile an inventory of sources of data that may be relevant to the evaluations in their regions, including both programmes and documents/publications that may contain relevant information. To assure transparency in the process, this inventory should be open to public scrutiny. This will allow stakeholders to identify missing sources and also allow countries to review the proposed data sources that may relate to their national situation.

If a country would like to challenge or object to the inclusion of data or information from a particular source, a rationale and argument for this exclusion should be provided. In principle, data and information should be accepted during the reporting stage; however, countries should have an opportunity to critically evaluate the way in which data and information are reflected in the evaluation products during the review and endorsement of the regional reports.

Table 6.1: Examples of existing data storage facilities

Institute	Area of Expertise	Advantage	Disadvantage
Air data			
Norwegian Institute for Air Research (NILU)	Air monitoring data	Operating and developing monitoring databases for more than 3 decades; compile data from ca. 40 countries (Europe and Russia); data centre serves several other international programmes (AMAP, EMEP, OSPAR, HELCOM). Collaboration with data initiatives in Asia (EANET, Korea)	
Cooperative Program for Monitoring and Evaluation of Long-Range Transmission of Air Pollutants in Europe under Convention on Long-Range Transboundary Air Pollution (EMEP) (see NILU)	Synthesis of (regional) POPs data	Eurasia focus; all European countries plus Russia. Hemispheric transport and modelling activities	
Human milk/blood data			
AMAP human health group / Institut National de Santé Publique du Québec	Human tissue monitoring (blood and breast milk)	AMAP Human Health sub-programme data (Arctic focus); CHUQ coordinates QA/QC inter-comparison programme for laboratories involved in human blood monitoring (ca. 20 countries, Arctic, Europe, North and South America)	Data management activities targeted only to AMAP assessment needs at present
GEMS/Food	Human tissue monitoring (breast milk)		Data management activities in support of WHO breast milk surveys

Institute	Area of Expertise	Advantage	Disadvantage
Other GMP media – marine (biota, sediments)			
International Council for the Exploration of the Sea (ICES)	Marine monitoring data (abiotic/biotic)	Operating and developing monitoring databases for more than 3 decades; compile data from ca. 20 countries (focus on NE Atlantic region); data centre serves several other international programmes (AMAP, OSPAR, HELCOM). Reporting systems include internationally adopted coding systems and reporting of methodological and QA/QC information.	Reporting formats are detailed. Complexity of reporting formats has deterred reporting from some countries and potential data sources.
Other GMP media – freshwater, foodstuffs			
National Water Research Institute, Burlington, Canada	Freshwaters	Data centre for the UNEP GEMS/Water (Global Environmental Monitoring System/ Freshwater Quality Programme; global (ca. 70 countries)	Freshwater media are not GMP priority; mainly physical/water quality parameters for major rivers
GEMS/Food			
University of Alaska-Fairbanks (SYNCON)	Data management	AMAP Terrestrial/ Freshwater data centre (Arctic focus); Flexible data reporting systems; online database	Current status of operations?

6.9 References

USDA Pesticide Data Program <http://www.ams.usda.gov/science/pdp/Qc10.pdf>

JECFA recommendations <http://www.inchem.org/documents/jecfa/jecmono/v48je20.htm#3.2.3>

ICES Environment data centre <http://www.ices.dk/env/index.htm>

ICES Reporting format <http://www.ices.dk/env/repfor/index.htm>

AMAP data collection <http://www.amap.no/>

UNEP GEMS/Water <http://www.cciw.ca/gems/gems.html>

Canada NPRI http://www.ec.gc.ca/pdb/npri/npri_home_e.cfm

7 STRATEGY, PROCESS AND DRAFT STRUCTURE FOR REGIONAL MONITORING REPORTS

7.1 Introduction

The purpose of this chapter is to outline the main tasks that must be completed in relation to implementation of the global monitoring plan for effectiveness evaluation. It is focused on fulfilling the minimum requirements for effectiveness evaluation and sets out actions, modalities and responsibilities for the completion of the work. It is intended to be a living document that will evolve to meet the needs of the global monitoring plan. Implementation of the global monitoring plan for effectiveness evaluation is dependent on availability of the necessary financial resources.

7.2 Implementation of the effectiveness evaluation

7.2.1 Minimum requirements for effectiveness evaluations

The Conference of the Parties has determined that the minimum requirements for effectiveness evaluation are that:

- The first monitoring report provides baselines for further evaluations;
- Air monitoring and human exposure through human breast milk or human blood would be used as core data;
- Water is the core environmental matrix for monitoring PFOS;
- Such comparable and representative core data should be obtained from all five regions;
- Guidance on standardization should be updated as needed;
- The strategic arrangements and partnerships established in the first evaluation should be maintained and extended, as appropriate;

Reports are prepared for the Conference of the Parties summarizing and presenting the data on a regional basis at intervals determined by the Conference of the Parties.

7.2.2 Identification and evaluation of potential sources of core media data for the monitoring report for effectiveness evaluation

Air monitoring and human exposure through breast milk or human blood will continue to be used as core media data and comparable and representative core data should be obtained from all regions. Data will be derived from:

- Existing international and regional programmes and activities;
- Existing national programmes and activities;
- National or regional arrangements and activities enhanced or initiated as a function of capacity-building to address regional data gaps.

The following sections describe how arrangements are being made to obtain information from these three potential sources.

1. Review of existing programmes, information or data and capacities related to the core media in all regions

The programmes identified for the first evaluation (see document UNEP/POPS/COP.3/INF/15) should be continuously reviewed to ensure their feasibility for subsequent evaluations.

2. Use of criteria to evaluate programmes and capacities in all regions related to the core media data

The criteria used for the first evaluation should continue to be used and reviewed as appropriate.

3. Continued identification of potential monitoring programmes and capacities for contributing to data production for effectiveness evaluation

The criteria used for the first evaluation should be applied as before to categorize programmes and activities into the following groups:

- Group 1: Programmes which can immediately provide information for the monitoring reports to be prepared for effectiveness evaluation;
- Group 2: Programmes that, with identified capacity enhancement, can provide information coverage in areas that would otherwise be inadequately represented in the monitoring reports;
- Group 3: Programmes which may be enhanced with capacity-building for future evaluations;
- Group 4: Programmes for which more information would be needed before categorization.

This categorization assists in the identification of areas where arrangements can be made with existing programmes to provide information and where identified levels of capacity enhancement can improve geographical coverage of information. The categorization will be continuously elaborated and updated at the regional levels through the application of the criteria and will form the basis of decisions on the data gathering activities to support effectiveness evaluation.

7.2.3 Guidance on standardization

Modalities: The guidance on the global monitoring plan for persistent organic pollutants should be applied and reviewed and updated as appropriate.

7.2.4 Development of strategic arrangements and partnerships for the acquisition of core media data for monitoring reports

The strategic arrangement and partnerships established in the first evaluation should be maintained and where feasible strengthened.

7.2.5 Regional organization groups and networks

The strategic arrangements developed in the regions should be maintained and updated as necessary.

Regional networks for implementation of the global monitoring plan should be maintained and extended as appropriate to facilitate data generation.

Parties will continue to report flexibly through the five United Nations regions. For monitoring programmes that cover more than one United Nations region the results will be reported through one of the United Nations regions and the other involved United Nations regions will be informed. Information from the Arctic and Antarctic will be incorporated in the appropriate regions taking care to avoid overlaps between regions.

The maintenance of the networks will be the task of the regional organization group which also agrees upon and oversees modalities for providing the comparable environmental monitoring information required by the Conference of the Parties for effectiveness evaluation. The elements considered in the first evaluation should be applied as appropriate.

Element 1: Establishment of the regional organization groups and networks

Modalities: The regional organization groups used for the first evaluation should be maintained. The members of the groups shall include the three members who will serve on the global coordination group plus up to three additional members, as well as invited experts in relevant fields, as necessary. The groups in cooperation with the Secretariat will set up appropriate arrangements giving due consideration to the existing capacities in each region for the establishment and or maintenance of the organization groups and networks in the regions as described above. The groups will use appropriate working arrangements, including electronic means as much as possible, to keep their networks for the production of regional monitoring reports. They will nominate members of the global coordination group. If a member needs to step down, Parties from the region in question should be invited to nominate a new member according to the procedure outlined in paragraph 4 of Decision SC-3/19. The terms for the members of the regional organization groups and the global coordination groups should

be at least from the start on an evaluation until that evaluation is finished and has been reported to the COP.

Element 2: Regional identification of existing national and international programmes or activities that can, or may with specified capacity enhancement, contribute to effectiveness evaluation

Modalities: The regional organization groups, with the aid of the Secretariat, will elaborate on the work of the groups for the previous evaluation to identify additional possible contributing programmes from each region. These elements may be subject to continued revision. The regional organization groups should continue to plan and implement step-by step capacity enhancement for Parties on a regional basis;

Element 3: Selection of those programmes and activities that should be adopted for contributing data and information for each region for monitoring reports and effectiveness evaluation

Modalities: The regional organization groups, with assistance from the Secretariat, will make an update of the possible contributing programmes using the selection criteria outlined in Annex I. The collective output of the regional groups will be a mix of existing programmes and activities that can deliver the required data and information without enhancement and those that could contribute following a specified degree of capacity enhancement. The regional organization groups will review these programmes in terms of the degree of regional coverage and decide upon the regional capacity enhancement that should be achieved for the monitoring report. The modalities used for the previous evaluation will be reviewed and applied as determined by the regional organization groups to reflect current regional conditions.

Element 4: Verification of the conformity of possible regional programmes with the methodological guidance for achieving the necessary levels of comparability of data (see also section C above)

The guidance document on the global monitoring plan will be applied as before. The data acquired in the framework of the global monitoring plan must enable a distinction to be made between variability representing true changes in the levels of persistent organic pollutants over time and differences that reflect variance derived from sampling and analytical procedures.

Modalities: A regional implementation plan built on the plan for the previous evaluation will be prepared by the regional organization groups to ensure that only data and information that satisfies the guidance document requirements for data comparability are used for the monitoring reports. The regional organization groups should also endeavor to supplement the core data with data from other media such as biota, water, soil and sediments, as appropriate, including community based participatory research data.

Element 5: Identification of how data and information may be stored and accessed including the possibility of developing a regional data warehouse

Modalities: Some key elements outlined in the guidance document are highlighted below:

- The possibility of using existing thematic data centres and of using those to serve more than one region will be explored;
- Tables produced to summarize the regional distribution of technical capacity may be modified to identify possible thematic data centres and strategic partners for such elements as data handling and regional coordination. This information may assist regional experts. Questions may be added to future capacity questionnaires to identify more effectively the availability of those institutions potentially able to accommodate data storage.

Element 6: Provision of data and information for the monitoring report and the establishment of appropriate arrangements

Modalities: The regional organization groups and the Secretariat will work to enhance the core comparable representative dataset from all regions by maintaining and extending regional monitoring network arrangements for the collection of core data through either, or both, of the following:

- International collaborative programmes, for those Parties that wish to follow this approach;

- Parties that wish to contribute nationally to the identification of capacities and regional data gaps, taking account of the work undertaken so far;
- In addition, the regional organization groups will, when appropriate, set up a regional process to supplement existing core data to address regional gaps in existing monitoring activity and capacity.
- Opportunities will be taken, where feasible, to maintain and extend strategic arrangements and partnerships, including with the international health sector and by developing collaborative twinning arrangements with other countries or with international monitoring organizations. Specific modalities include:

Organization of arrangements with Parties and non-Parties that possess capacity and capability to provide comparable monitoring data on the core media;

Organization of arrangements with existing international programmes (regional and global) that can provide comparable monitoring data on the core media relevant to effectiveness evaluation. This work would not be subject to capacity-building support except when it is related to assisting Parties and or regions without capacity to participate in those programmes;

Organization of arrangements in regions without the necessary capacity to contribute to a global monitoring plan as envisaged by the Conference of the Parties. This work would be expected to require capacity-building support.

Element 7: Planning and implementing regional capacity-building that may be necessary to implement the agreed arrangements

Modalities: Some of the activities being carried out in terms of planning and implementing regional capacity-building are set out below:

- The comprehensive regional inventory and analysis of capacities performed by the respective regional organization groups for the previous evaluation should be reviewed and updated as necessary, taking into consideration the specific regional conditions, information and knowledge.
- The generic plan for step-by-step capacity enhancement for Parties for the purpose of implementing Article 16 of the Convention used in the first evaluation should be reviewed and updated where needed. The needs and opportunities for capacity-building to increase participation in the global monitoring plan are to be taken into account during the implementation of Conference of the Parties decision SC-2/9 on technical assistance.
- In completing and continuing the work described above, the Secretariat will consult as appropriate and necessary with the regional organization groups and other relevant structures in order to continue to plan and implement step-by step capacity enhancement for Parties on a regional basis.

Element 8: Mechanisms for information collection for the purposes of the regional reports and for their preparation

In each region, data and information for production of the regional monitoring report will be derived from a variety of different sources (including global and regional monitoring programmes, as well as those of individual Parties and non-Parties). Each region will need to agree on how information from those sources can be accessed for the purpose of reporting to the Conference of the Parties.

The procedure used for the first evaluation should be maintained and updated as needed.

7.2.6 Summarizing and presenting data on a regional basis, to be used in effectiveness evaluations

Paragraph 2 of Article 16 states that the Conference of the Parties shall make arrangements to provide itself with comparable monitoring data on the substances listed in the annexes to the Convention, as well as on their regional and global environmental transport. There are therefore two objectives for the

arrangements, one concerned with the environmental levels of persistent organic pollutants in priority media and the other with their environmental transport.

1. Reporting on levels in core media **[FORMAT: move to next page]**

Article 16 does not suggest that the monitoring reports are to contain any interpretation or assessment on the significance of the levels in environmental media. In its decision SC-2/13, the Conference of the Parties refers to “summarizing and presenting the data on a regional basis”. With this understanding, successive data reports provided over a number of years will enable the Conference of the Parties to view changes over time, providing the data is of sufficient quality and precision.

Modalities: The regional organization groups, in consultation with the Secretariat, should take responsibility for preparation of the regional reports by each establishing a drafting team of experts. This activity can be undertaken with, for example, international programmes or individual consultants. The reports would follow the uniform outline agreed upon by the regional organizations groups for the first evaluation.

The regional organization groups may find it useful to consider the following issues when drafting the monitoring report for effectiveness evaluation:

- The proposed sampling window could be 200X +/- 5 years. 200X would be chosen with regard to the sampling period for the preceding evaluation;
- There could be options for providing additional information that is not obligatory under the Conference of the Parties decision, such as trend data prior to the evaluation in question;
- There may be ownership issues for some of the data (Governments vs. institutions vs. scientists). Data policy agreements should be considered when such situations arise.

2. Reporting on regional and global transport

The Conference of the Parties did not indicate its expectations concerning reporting on regional and global environmental transport for the first phase. To gain an understanding of the environmental behaviour (transport and fate) of the listed chemicals, a range of possibilities could be considered including:

- For persistent organic pollutants that are mainly transported by air (the “flyers”), global monitoring plan data can be assessed using information on atmospheric transport potential (for example, characteristic transport distances and knowledge of air currents, as outlined in the amended preliminary version of the guidance document).
- For those chemicals for which water transport is also important (the “swimmers”), global monitoring plan data can be assessed using information on ocean currents, potential riverine inputs and air-water exchange over large water bodies. This is especially relevant for the global monitoring plan data obtained in coastal areas. This may not be a key issue for the original list of persistent organic pollutants in Annexes A, B and C, given that the primary environmental movement of these particular substances is in the atmosphere. This may not be the case, however, for some substances that may be added to the Convention in the future.
- Back trajectory analysis (relatively simple in terms of data and infrastructure support), can be extended to generate probability density maps for improved interpretation of trend data with respect to temporal changes in advection inputs for global monitoring plan sites. The standardized approaches used for the first evaluation should be applied.
- The use of regional and global-scale models (more complex and demanding in terms of input data, although a range of such models is available). Global monitoring plan data can be used to initialize models and evaluate transport pathways across regional and trans-regional (trans-continental) areas.
- The coordination group could nominate a small team of experts to prepare a report or reports, based upon published literature and the data derived from the air monitoring component of the global monitoring plan. With this approach, interpretive techniques (such as modelling and

back trajectory analysis) would be a part of the reports reviewed by the experts, and not directly a component of the global monitoring plan.

- Involvement of and collaboration with current international efforts, such as the Task Force on Hemispheric Transport of Air Pollution under the United Nations Economic Commission for Europe Convention on Long-range Transboundary Air Pollution, AMAP or any other body studying global transport of persistent organic pollutants will assist the coordination group to evaluate data on regional and global environmental transport and related climate effects.

7.3 Draft structure of regional monitoring reports (to be modified for the use in the particular regions as appropriate)

Executive Summary

7.3.1 Introduction

It includes the objectives of Article 16 of the Convention and of the GMP. Reference should be made to the previous GMP phases.

7.3.2 Description of the region

- Overall composition of the region, political, geographical, links to POPs, industrial activities, agriculture etc.
- The regions - their boundaries and reasons for their selection; and,
- Sub-regional arrangements (*e.g.* identification and rationale for any sub-regions that may have been created).

7.3.3 Organization

The over-arching organizational strategy for the GMP and for the preparation of the regional monitoring report is as follows:

- Preparatory workshops, and internet based consultations and communications, possibly sponsored by the Secretariat and/or other donors;
- Establishment and responsibilities of the regional organisation groups;
- Agreement on a basic framework to provide comparable information;
- Regionally developed and executed implementation plans based upon the global framework.
- Information gathering strategy
- Brief description of the process and decisions taken to decide what information would be needed (regardless of whether or not there are pre-existing sources of that information), focusing upon the formation of the sampling matrix.

Strategy for using information from existing programmes

Summary information on linkages and arrangements to other programmes utilized as data and/or information sources.

7.3.4 Methodology for sampling, analysis and handling of data

Strategy for gathering new information

Explanation in the context of the sampling matrix regarding media, site selection, sampling frequency, and agreed protocols to preserve sample integrity (*e.g.* quality assurance and control, transport, storage, and sample banking). Identification of gaps and capacity development needs to fill them.

- Air;
- Human tissue (maternal milk and/or blood);

- Water;
- Other information relevant for the regional monitoring report (e.g. information from other matrices or historical trend data).

Strategy concerning analytical procedures

This will contain a brief description of analytical procedures used to ensure quality and comparability of data.

- Decisions taken regarding analytical techniques and comparability (including inter-laboratory exchanges);
- Protocols concerning extraction, clean-up, analysis, detection limits, and quality control.

Strategy concerning participating laboratories

- General description of the approach for classifying laboratories according to their instrumentation level;
- Description of the criteria for classifying laboratories, if used in the region, and identification of the laboratories involved.

Data handling and preparation for the regional monitoring report

- Agreed protocols for data acquisition, storage, evaluation and access;
- Statistical considerations;
- The information warehouse;
- Data from existing programmes.

7.3.5 Preparation of the monitoring reports

- Description of the arrangements put in place by the regional organisation group to oversee the production of the substantive regional monitoring report for that region;
- Identification of the roles and responsibilities of the drafting team of experts selected by the regional organisation group to prepare the report for that particular region.

7.3.6 Results

For each of the substances in Annexes A, B and C of the Stockholm Convention a brief description of the:

- Historical and current sources;
- Regional considerations;
- Other information (e.g., trends in environmental levels reported elsewhere).

The above would be useful in both text and table format. The text could be organized in a common sequence (e.g., cyclodiene insecticides; DDT; toxaphene; hexachlorobenzene; PCB; PCDD and PCDF).

The results in context

The first regional monitoring reports provide the baseline data for the effectiveness evaluation as first sets of available information on levels of the chemicals in Annexes A, B and C in the environment and human matrices (within the timeframe 2003, plus or minus five years). Where regional data gaps have been identified in the first regional monitoring reports for the reference timeframe, the first relevant regional information that becomes available will be used as baseline. For the subsequent monitoring reports, trend detection should be based on the relevant baseline information and subsequent

monitoring results. The identification of further data gaps (*e.g.* analytical, processing, storage capacity) and capacity development needs to fill them should be included.

Review of levels and trends in the regions

For the regional monitoring report, a presentation of resulting changes in levels of the Annex A, B and C substances in each of the media would be favored. This information would support the evaluation of trends for the effectiveness evaluation. The results could be provided in the following common sequence (cyclodiene insecticides); DDT; toxaphene; hexachlorobenzene; PCB; PCDD and PCDF). For PCDD/PCDF and dioxin-like PCBs the levels would also be expressed as toxic equivalents (TEQ). For each substance or group of substances resulting changes in levels of POPs will be presented in the following order:

- Air;
- Human tissue (maternal milk and/or blood);
- Water and other matrices if added to the guidance
- Other information relevant to the monitoring report (*e.g.* information from other matrices or historical trend data).

Information concerning long range transport

See options in section 7.2.6 of this guidance document.

7.3.7 Conclusions and Recommendations

The aim will be to provide a clear and concise synopsis of the results of the Global POPs Monitoring Plan for the use of the Conference of the Parties when it undertakes the Article 16 effectiveness evaluation, including the relevant scientific information *e.g.* changes in levels, but also including a brief statement on regional data gaps and capacity needs.

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8 ENVIRONMENTAL SPECIMEN BANKING

8.1 Introduction

Environmental Specimen Banking is an activity to collect and keep “representative” environmental and human samples (specimens) for long-term, typically several decades, without changing their chemical compositions and properties, including variety of pollutants accumulated in the specimens (Becker et al., 2006). “Representative” means well-described environmental samples commonly or widely present in the environment so that temporal and / or spatial trends will be revealed by the analysis of the pollutants in the archived samples in future. Selection and collection of the environmental samples should be designed carefully so that minimum set of archived samples will provide us with general, unbiased view of the environmental levels of the pollutants. This is basically an identical procedure to design and conduct environmental monitoring itself (see Chapter 3 Statistical Considerations and Chapter 4 Sampling and Sample Preparation Methodology). As Environmental Specimen Banking is aiming to support not only the present but also the future activities under the Convention as described later, however, the banking activity is expected to have a wider scope than that covered under the present GMP.

Environmental Specimen Banking has been acting vital roles in many countries, such as Sweden (Odsjo, 2006), Canada (Wakeford and Kasserra, 1997), US (Becker and Wise, 2006), Germany (Federal Ministry for the Environment, Nature Conservation and Nuclear Safety, 2008) and Japan (Morita et al., 1997; Shibata et al., 2007; Tanabe, 2006), for decades to support environmental monitoring activities. There are many environmental specimen banks that also include human samples, among which some have been operated for human biomonitoring of chemical exposure (Gunter 1997; Becker et al., 2006; Wiesmüller et al., 2007; Koizumi et al., 2009). Environmental Specimen Banking is expected to play a key role to support POPs monitoring under the GMP of Stockholm Convention (UNEP/POPS/COP.4/31). By the systematic storage of part of the environmental samples collected for monitoring purpose, each Party will be able to analyze the samples in future to assess the quality of the previous analytical data, to get quantitative data for previously “not detected” or unattended compounds by more advanced analytical methods, to get baseline data for newly added POPs, to reveal temporal and / or spatial trends of POPs / newly listed POPs / POPs candidates, and to identify new / emerging pollutants. As an example, Figure 8.1 shows temporal trends of PFOS and other perfluorinated surfactants levels in mother’s milks from Stockholm, Sweden, which were archived in a specimen bank at the Swedish Museum of Natural History. Temporal / spatial trend data will be very helpful in the review process of proposed chemicals to the annexes of the Convention, and also in the effectiveness evaluation process. Furthermore it is expected to support implementation of the Convention, particularly in developing countries, by realizing earlier start of the sample collection and storage while the analysis will be conducted after the relevant capacity building / enhancement procedure will be completed.

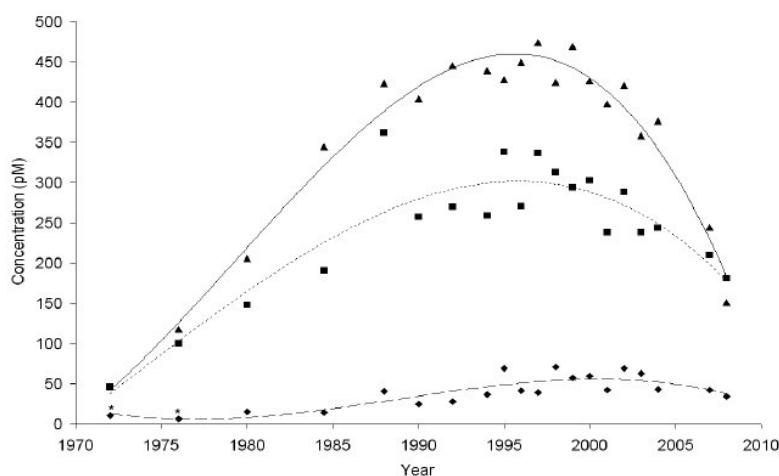


Figure 8.1: Concentration (pM) of PFOS, PFOA and PFHxS in mother’s milk from Stockholm 1972-2008 (Sundstrom et al. 2010).

In addition to the above roles to support the Convention, Environmental Specimen Banking is expected to play indispensable roles at the time of environmental incidents and disasters, *i.e.*, to assess the effect of disaster quantitatively and show the unaffected status before the disaster by the analysis of archived samples. Figure 8.2 shows temporal trends of benzo(a)pyrene levels in bivalves along the affected coastline after a tanker accident (Shibata, Y., 1998). Gray dots showed B(a)P levels of the archived samples in the area collected before the accident, indicating that B(a)P levels in bivalves, although increased two to three orders of magnitude after the accident, returned to the original level after several years. The bank will also provide us with key information regarding the past pollution status when adverse effects of pollutants having delayed toxicities being appeared decades after the exposure, such as carcinogen or endocrine disruptive chemicals, are suspected to occur.

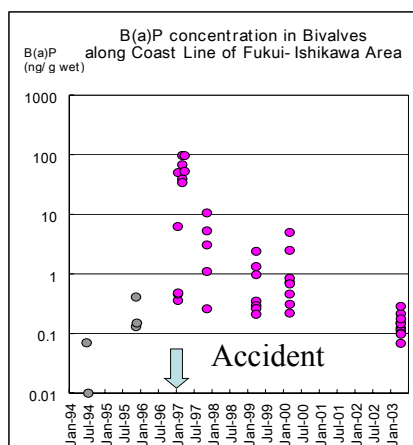


Figure 8.2: Benzo(a)pyrene levels in bivalve samples collected along Japanese coastline before and after a tanker accident (Jan 1997) (Shibata, 1998)

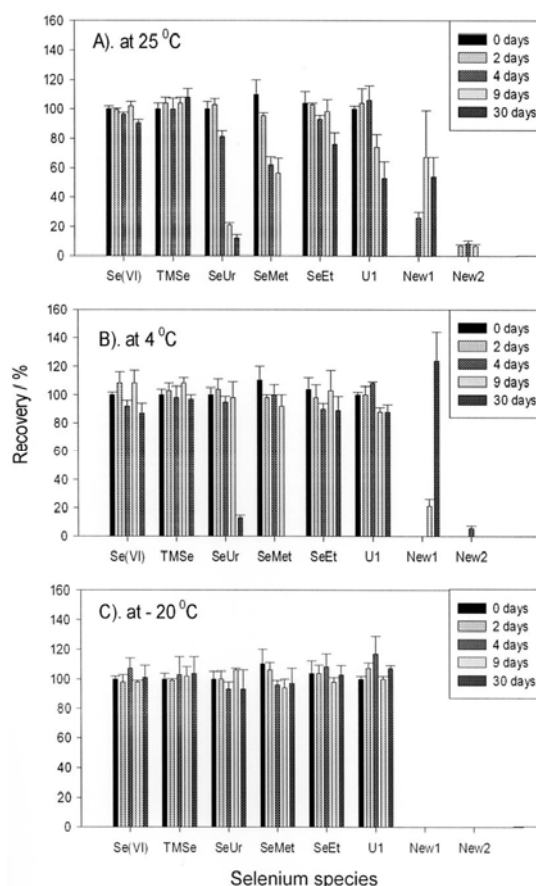


Figure 8.3: Stability of organoselenium compounds added to human urine at different temperatures. Selenourea was found to be least stable among the Se-compounds examined, but could be kept intact for 30 days at -20 °C (Zheng et al 2002).

Many of the Environmental Specimen Banking activities have high capacity and capability to produce large amount of homogeneous materials in terms of chemical composition as well as to analyze variety

of pollutants, and are sometimes accompanied with the production of reference materials for QA/QC of the environmental analysis (National Institute of Standards and Technology, USA, National Institute for Environmental Studies, Japan, etc.). Thus the Environmental Specimen Banking is expected to support GMP of the Stockholm Convention not only by archiving monitoring samples but also by building / enhancing analytical capacity.

8.2 Basic Concept and Requirements

8.2.1 Basic concept of Environmental Specimen Banking

Environmental Specimen Banking is basically a highly conserved operation to be continued for long term without changing fundamental procedures in order to secure sample comparability and chemical properties / integrities. Therefore the whole procedure, including type of samples, sampling locations, amount of stored samples, transport procedures, sample homogenization procedure and homogeneity check, sub-sample portioning and storage method, and storage facility maintenance etc., should be carefully designed, operated and recorded. Detailed description of each procedure, manuals or SOPs for the procedure, and periodical up-dating of these manuals are necessary for the proper operation of the banking. Also detailed information on the sampled organisms and/or individuals, samples itself, including sampling procedures and sample handling, will be very important and should be recorded carefully (Table 8.1). In other words, the stored samples should have enough supplemental information for later statistical analysis and correct interpretation of the results as well as for ensuring “traceability”; *i.e.*, quality and quantity of accompanied data will change the value of the sample.

Table 8.1: Additional information that could be stored in connection to the stored samples.

<Human Samples>
Age, gender
Weight, height
Information on living place, occupation, other questionnaire data
Date of collection, location
Type of sample, Volume
Sampling procedure, transport, sample processing records
Fat contents, other clinical examination results
Results of the POPs analysis
<Atmospheric samples>
Date of collection, location
Air volume, sampling period
Climatic data
Sampling procedure
Pre-cleaning, transport, other processing records
Responsible person, source of additional information

8.2.2 Samples to be stored

Under Stockholm Convention, the primary target of samples for storage will be those selected as priority monitoring media under the Convention, including air (filters or adsorbents) and human samples, *i.e.*, breast milk and / or bloods. An additional media, water (filters, passive sampling adsorbents), is being considered for the monitoring of PFOS and HCHs (see Chapter 4.3). As the banking will support the future activities under the Convention, however, it is expected to have wider scope than the present GMP. Therefore some general aspects of the Environmental Specimen Banking will be included in this section.

Environmental monitoring may include several different concepts; *i.e.*, to know concentration of pollutants in different environmental compartments (to know sources, levels, and chemodynamics of pollutants, or to check clearance status of environmental criteria / standards), to reveal exposure status (exposure monitoring for risk assessment and control), and to evaluate adverse effects of pollutants to wildlife / human beings (effect monitoring) (see, for example, Rüdél et al. 2009, for concepts of environmental monitoring). Biological samples are preferred for banking because they tend to accumulate chemicals like POPs in higher concentrations through food web, and also their levels are time-integrated due to long half-life within the body. Thus a small amount of biological samples collected once a year, for example, may provide us with representative levels of POPs (pollution

levels, or exposure status) in an area. If instead water or air samples are collected, a much larger amount of samples collected frequently in short interval will be needed to get comparably reliable view of their environmental levels and the temporal trends. In addition, biological samples will potentially provide us with information on the effects of pollutants to wildlife / human beings, *i.e.*, suitable for effect monitoring.

Biological samples for the banking may be classified into the following three groups; 1) common, short-lived organisms in lower trophic level, such as fishes (particularly small ones feeding on planktons) and bivalves, which is suitable for revealing detailed spatial / temporal trend analysis, 2) long-lived, higher-trophic level organisms, typically top-predators like fish-eating birds (or their eggs) and marine mammals, which are sentinel species to POPs by accumulating them higher than other species in lower trophic levels, and 3) human samples. Group 1) will be useful for periodical (yearly) monitoring of pollution status to know their temporal trends, while Group 2) may be used for assessing risk of POPs pollution in a selected ecosystem / environment. Human data will primarily be used for assessing risk of chemicals to humans and identifying priority of regulation. Other types of specimens for the banking include soil, vegetation, sediment cores and / or other environmental samples with annual ring / layer structure (Becker et al, 2006, and references therein), and bark pocket of trees as a time capsule for the past environment (Satake et al., 1996). Time-integrated type of air or water samplers, such as passive air sampler, may alternatively be collected and kept for the purpose (Table 8.2).

Table 8.2: Samples suitable for banking.

Low trophic level organism	Useful for periodic monitoring of local pollution status
High trophic level organism	Useful for risk assessment of POPs pollution in an ecosystem
Human samples	Useful for human risk assessment and priority of regulation
Other media, such as soils, sediments, vegetation	Useful for periodic monitoring of local pollution status, their trends and understanding environmental chemodynamics of chemicals
Filters, adsorbents and their extracts of air, water	Useful for background monitoring, and understanding long-range transboundary transport of chemicals

Human samples suitable for POPs analysis are breast milk and bloods (see Chapter 4.2). Other media used for environmental monitoring include urine, hair, saliva, umbilical cords, etc. Urine samples have been used extensively for the analysis of metabolites of POPs or other chemicals of concern.

8.2.3 Long-term storage method

Cryo-preservation techniques, including electric freezers, cold rooms and liquid nitrogen freezers, have been employed for the long-term storage of various environmental specimens. Some type of specimens, such as air-dried soils and sediments, wood and seeds, bone, feathers, hair and nail, can be preserved at room temperature. Wet samples of biological origin, however, should be kept frozen for long-term storage. Freeze-dried samples may be kept at higher temperature (for example 4 °C) for long-term, although freeze-drying process might cause loss of relatively volatile chemicals and contamination by oil vapor etc. Even air dried samples, including human umbilical cord kept at ambient temperature for long term, have been successfully used for exposure assessment to POPs or heavy metals accumulated during pregnancy (for example, Nagayama et al., 2011).

There are apparently no general criteria of the storage temperatures for the bank, though several different temperatures have been selected historically for different purposes (Table 8.3). Generally speaking, samples will be kept better under lower temperatures (Zheng et al., 2002). Biological

samples at liquid nitrogen temperature (-196°C), or in liquid nitrogen vapor phase storage facility (around -150 to -160°C), will be stable and chemically unchanged for decades while those kept at -20°C tend to be deteriorated to some extent in a decade or two as desiccation and metabolic degradation are not ignorable at the temperature. Deep freezer at -80 or -85°C , the temperature originally set for storing dry-ice, have been used extensively in many banks and for other purposes, and are proven to be useful for the long-term preservation of many types of samples. Another temperature, around -60°C , is frequently used commercially for the large-scale storage of fishes and meats, and is proven to be also useful for storage of biological samples. Techniques for construction and maintenance of large refrigerated warehouses under -60°C have been established, and a large capacity of this type of storage is available now around fishing ports / air ports / other hub of transports in the world.

Table 8.3: Temperatures used for banking of specimens.

Room Temperature		Dry samples, such as soils, vegetation, bird egg shells, hair
-20 degrees of Celcius		Biological samples, sediments etc. for heavy metals, POPs analysis (not suitable for long-term)
-80 / -90 degrees of Celcius		Biological samples, sediments for long-term storage; useful also for biochemical analysis
-160 / -196 degrees of Celcius		Biological samples; chemically most appropriate for long-term storage

It has, however, to be considered that electric freezers will need costly regular maintenances of the mechanical refrigeration parts (Owen and Woods, 2008). Furthermore, measurable recrystallization processes within water may occur at temperatures above -130°C (Eisenberg and Kauzmann, 2005). Therefore, the best available method is to keep samples under vapor phase of the liquid nitrogen because of the lower temperature (typically around -150 to -160°C) under oxygen-free condition. Though such a system tends to cause high investment costs, it may be cost-effective in the long run, depending on the amount of stored samples and availability of liquid nitrogen and its cost. In addition, the liquid nitrogen cooling system will keep samples at low temperature more robustly / securely than electric freezers / cold rooms at the time of disaster. At the Great East Japan Earthquake in March 2011, loss of electricity for three days threatened the archived samples in the Environmental Specimen Bank at the National Institute for Environmental Studies, Japan (Tanaka et al., 2012). The temperatures of all liquid nitrogen freezers were kept at -160°C due to remaining liquid nitrogen in the bottom of the tanks, while the temperature of large cold rooms operated at -60°C was gradually increased to -47°C during the three days. The temperatures of -80°C freezers, on the other hand, increased to nearly zero $^{\circ}\text{C}$ only after a day, and dry-ice blocks had to be put into the freezers every day during the period of electricity loss in order to keep the samples frozen. It is important to set up emergency operational procedures in order to keep samples against such rare but disastrous events.

Note that sample storage for chemical analysis reported in this chapter is different from storage of cells / genes for biomedical application where chemical integrity of the sample will not be considered to be preserved.

8.2.4 Facility requirement

Environmental Specimen Banks may consist of low temperature storage facility, sample processing room, sample analysis room, and data storage and analysis facility. To ensure secure long term storage of valuable samples, arrangement of some back-up systems, like extra storage facility needed for accidental trouble of the used freezers, and back-up generator or CO_2 / liquid nitrogen supply line against a short term electricity shutdown, are vital. Size and temperature of the storage facility (from a single freezer to several large cold rooms or a series of liquid nitrogen freezers) is highly variable according to the type and amount of collected samples for storage, and / or available resources. It should be noted that even a couple of freezers will be very useful and play important role together with

well-designed environmental monitoring activity, especially for human bio-monitoring where limited amount of valuable human samples, such as breast milk or bloods, will be collected. Note that repeated thawing – re-freezing process will damage the sample and change its chemical composition (Zheng et al., 2002). It is therefore recommended to keep as small as possible amounts of samples separated into aliquots so that several chances of retrospective analysis will be provided in future by using more advanced technologies. Moreover, the necessary amount of biological material for chemical analysis can be assumed to further decrease in the future.

It is also recommended to have sample analysis capability together with storage and processing facility in order to regularly check homogeneity of the samples, “cleanness” of the facility, and ensure “free of contamination” during sample collection, transport, processing and archiving. Usually homogeneity is checked by some chemical analysis. It is checked in two ways, *i.e.*, within the tube and between the tubes, typically by the analysis of several elements, including minor and trace ones. As for contamination check during the sample handling, many different chemicals may be analyzed, and a series of analytical instruments are required for proper operation of the facility.

Chemicals of concern for environmental / human monitoring may include many industrial chemicals, such as surfactants (including PFOS), flame retardants (including brominated flame retardants) and other plastic additives, which have been used extensively in the production of many commercial products. It should be noted that there are many chances of contamination by these chemicals during sampling, transport and processing before final start of long term storage, and careful and regular monitoring of the whole process is very helpful for meaningful retrospective analysis in future. Some example of contamination include; elements (alkali metals, boron, arsenic etc.) from glassware, perfluoroalkyl carboxylic acids from fluoropolymer products, materials (such as bisphenol A) or additives (such as phthalate esters, alkylphenol ethoxylates) or flame retardants (such as polybromodiphenylethers, polybromobiphenyls, chlorinated paraffins, organophosphorous compounds, antimony, etc.) from plastic wares, furniture and construction materials of the building. It is recommended that some “blank” samples, for example purified water, for checking whole contamination during sampling, transport and processing, will be analyzed and also stored periodically together with environmental samples, so that chemicals found in a future retrospective analysis can be assured to be originally contained within a sample rather than added, or produced, during sample handling procedure (Shibata et al., 2007).

8.2.5 Administrative system

A group of people with different tasks will be needed for proper operation of the banking. The tasks may include sample collection / receipt, sample processing, checking homogeneity / other properties of the samples, management and maintenance of sample storage equipment (and analytical laboratory), data management and database maintenance, and managers (supervisors and director) of the whole operation. Collaboration of people with several different professional backgrounds is needed. Frequently the banking is operated together with systematic long-term environmental monitoring; in such cases, support and guidance by the professional scientists / technicians in several related fields, such as analytical chemists, atmospheric chemists, biologists and / or medical doctors, will be expected and valuable for efficient operation of the banking.

Establishment of sample tracking and data management systems are also required. A manual record may be sufficient in case of sample banking by a single freezer for pooled human samples, while more sophisticated systems based on, for example bar-code system together with PC-based software, may be useful for identifying, tracking and keeping records of the samples in case of large facility archiving several long-term environmental monitoring samples. The simplicity / complexity of the system may reflect the size / scale of each bank, but transparency, security and robustness are among the important issues to keep sustainability of the program.

8.2.6 Safety caution and training

Usually homogenization uses some mechanical system, which might cause accidental injury during operation. Use of dry-ice or liquid nitrogen for sample freezing or cryo-homogenization procedure, might cause “frostbite” when directly touched to skin or other parts of the human body. They should not be used or stored in closed, or poorly ventilated room for long term because they produce either CO₂ or N₂, both of which may cause “suffocation” accident. Never keep dry-ice in a cold room! In addition to keep good ventilation, oxygen sensor – alarm combination is recommended in a cold room,

or other places, such as sample processing room, where large emission of CO₂ or N₂ is anticipated. Never touch frozen samples / containers / walls / shelves with naked hand / other part of skins directly. When you touch them with your wet hand, the moisture on the hand is instantaneously frozen and fixed your hand to the cold surface, thereby damaging your skin severely. Also some dangerous chemicals, such as strong acids, methanol and other organic solvent with either toxicity or flammability, may be regularly used during the operation. The handling of these chemicals, including waste management, should follow the established scheme in each laboratory, and prior and regular training / teaching of the technical person together with the regular health check on the relevant terms should be conducted to prevent accident and ensure the sustainability of the program.

Care should be paid to prevent accidental contamination of samples during processing. Usually clean groves and clothes are warred to minimize contamination (and also for safety reason) during handling samples. It should be noted that these wares themselves may cause contamination of some specific chemicals, such as plasticizers included in polyvinylchloride products and musk or surfactants in detergent used for washing wares.

Human samples, such as blood, serum, plasma, breast milk and urine, may contain pathogenic microbes, such as virus or bacteria, which might cause human diseases, and thus should be carefully handled in order to prevent accidental infection. It should always be kept in mind that storage of human samples, or even other environmental media, such as wildlife and sediments, might potentially be a process of preserving pathogens to human or wildlife, and that biohazard protocols during collection, specimen handling and processing, and banking should be developed so as to minimize exposure. Cryo-homogenization and storage process may stop multiplication of the microbes, but not destroy them. Use of disinfectants, such as UV light and anti-microbes, may be useful to keep the clean environment but may change chemical composition / integrity of samples. Aqueous ethanol may be an alternative choice for disinfection. For certain bio banks archiving human samples measures according to national biosafety regulations may be necessary. The above caution, on the other hand, means that banked specimens, if properly designed and operated, will be useful to reveal not only pollution history but also other issues including spread of diseases in human or wildlife community.

8.2.7 Sample access / discarding policy

Another important issue for operating the bank is to determine sample access policy, and the limit of term the samples will be kept; in other words, sample discarding policy. As the amount of sample is limited, usage of the samples should be conducted under careful consideration. On the contrary, due to limited storage capacity and expensive cost of long-term storage, the stored amount should be kept minimized. Prioritization of stored samples, therefore, is needed; issues to be considered may include purpose of the storage, amount of samples, storage period, the quality and quantity of accompanying information, and quality of the samples themselves. Many of the banks set sample access policy and open gate on the application by researchers outside of the bank for the analysis of many different types of pollutants. The analytical data will add further value to the stored samples. Ethical issues have to be considered during accessing / discarding human samples, too.

8.2.8 Guideline, manuals and Standard Operational Procedures

Many of Environmental Specimen Bank facilities have made Standard Operational Procedure (SOPs) for the sampling and / or storage procedures, and some are made available through websites or other means. The International Society of Biological and Environmental Repositories (ISBER) provides an international forum that addresses the technical, legal, managerial, and ethical issues relevant to repositories associated with biological and environmental specimens. Through member contributions, ISBER has developed and published the 2012 Best Practices for Repositories: Collection, Storage, Retrieval and Distribution of Biological Materials for Research document (Campbell et al., 2012). The third edition of this Best Practices document provides a practical guide and suggested 'best practices' from repository professionals for the management of specimen collections and repository facilities. The document is divided into 13 sections and also includes 3 appendices with detailed information on the following:

- A: Repository Planning Considerations
- B: Facilities
- C: Storage Equipment and Environments

D: Quality Management

E: Safety

F: Training

G: Records Management

H: Cost Management

I: Biological Material Management

J: Packaging and Shipping

K: Specimen Collection, Processing and Retrieval

L: Legal and Ethical Issues for Biospecimens

M: Specimen Access, Utilization, and Destruction

References

Appendix A: Internet Resources

Appendix B: Glossary

Appendix C: Abbreviations

8.3 Sampling and Storage

Sampling process should follow the guidance of GMP under Stockholm Convention (see Chapter 4). Here a brief caution on the vessels and devices used for the sampling, processing and storage will be summarized.

8.3.1 Sampling devices

Among priority media in Stockholm Convention, human samples, *i.e.*, breast milk and bloods, would be preferably kept individually rather than as pooled samples if informed consent for the detailed epidemiological studies in future was obtained at the time of collection and enough space for long-term archiving were available. Archiving pooled samples, on the other hand, will need minimum space and costs, and still be very effective to support the monitoring activity; for example, a single freezer in a hospital will be sufficient to keep pooled human breast milk samples for years. Additional information, such as sample weight, sampling date and location, sampling system etc., should be recorded and kept together with the samples.

In Environmental Specimen Banking activity, samples are kept for future analysis of newly emerging chemicals in addition to the present target of regulation. This means that ideally the whole process, from sampling to storage, should be designed to prevent / minimize contamination by any chemicals / elements which are not of concern at present. Furthermore, it is important to keep detailed record of sampling / processing / storage devices because potential contamination or other biases might be produced by these devices. For example, blood collection tube, syringe and needle are coated with various chemicals, including silicone oil and polymer surfactants, the detailed chemical constitution of which are frequently not open, being protected by patents (Shibata et al., 2011). Some chemicals are derived from the original material (such as plasticizers, flame-retardants or other additives in polyvinyl chloride (PVC) or other plastics), some are added intentionally (for example, coating polymer on polyethylene terephthalate (PET) surface of vacuum collection tube to prevent adhesion of clotted red blood cells) while others are being contaminated during production of the materials (for example, perfluorinated chemicals used as detaching reagent in molding process of plastic wares / elastomers). Some elastomers used for syringe plug contain metals, such as zinc. Serum separators used to separate serum (or plasma) from blood cells by centrifugation contain hydrophobic chemicals and were reported to absorb hydrophobic pharmaceuticals (Bowen et al., 2005). POPs might be adsorbed to the separator, too. It is recommended to keep record of the producer, brand and type of devices used for sampling etc., and also to keep unused blank tubes / syringes etc. together with the samples in order to assess future analytical data properly.

Air and water samples themselves are generally not suitable for banking due to large volumes necessary for trace pollutant analysis as well as suspected instability of chemicals that might be lost by

adsorption to container wall etc. during long-term storage. Some archiving activities of these matrices have been seen in special cases, for example Cape Grim Air Archive, in which air samples have been kept in flasks for major, minor, trace gases as well as stable VOCs analysis (O'Doherty et al, 2009). Usually, however, the filters, adsorbents, or extracts, may be more suitable for future retrospective analysis of chemicals. An illustrative example is monthly collection and archiving of airborne particulate matters on quartz fibre filter collected in central Tokyo; the archived filters were used to reveal temporal trends of dioxins (Matsumura et al., 2002, 2003) and polycyclic aromatic hydrocarbons (Ezoe et al, 2004) for two decades from 1980. In a passive air sampling programme (GAPS), the extracts from the adsorbents were divided into two and one part was kept in sealed glass ampules for future retrospective analysis. Duplicate sampling by passive air sampler and archiving a set of adsorbents may be an alternative choice. Detailed record on the sampling dates, storage devices, materials used, etc., should be kept together with the samples. Filters and adsorbents should be pre-cleaned according to the sampling SOPs. It should be noted that even sampling device, such as high volume air sampler, might cause unexpected contamination from the materials used to construct the device; typical examples are perfluorochemicals in fluoropolymer products / coatings, and flame retardants and their impurities used for plastic / elastomer products (Takasuga et al., 2012).

8.3.2 Sample processing and archiving

In the case of human breast milk or blood samples, several portions of a sample will be kept in the storage tubes after gentle mixing procedure. Sample size will depend on the situation, but will be minimized but sufficient for one-time analysis of some particular chemicals/elements. Note that freezing process may cause precipitation of some materials, including fats, or hemolysis, which might affect homogeneity of the sample at the time of portioning. In some cases, sample processing for banking might involve separation of specimen components, such as plasma or sera for the analysis of organic contaminants, from the whole samples, like whole blood for the analysis of trace elements. In such cases, care should be taken not only to assure sample homogeneity but also to prevent / minimize contamination of target chemicals during the process (see 8.3.1). Pooled human samples are thought to represent pollution status of a population in an area, and are very efficient in terms of both the analytical costs and the banking facility. Liquots of pooled human breast milk samples collected and analyzed at the 1st effectiveness evaluation procedure (joint WHO/Stockholm Convention programme) were kept in a freezer and are now used for the analysis of additional newly listed POPs. Pooled samples, however, have disadvantages compared with individual samples (see Chapter 3.5).

In the case of biological and soil/sediment samples, homogeneity is an important feature of the archived samples to ensure that future analysis of a small portion of the sample will provide us with “representative” information on the pollution status of the period. Variety of homogenizing techniques have been developed and applied to the Environmental Specimen Banking activities, including mixer, blender, chopper, crusher, ball mill, rod mill, and cryo-homogenization. Usually a hard material, such as metals and ceramics, are used for crushing/ homogenization procedures. In some cases, plastic materials, like fluoropolymers, have been used as a cover or coating material for mills. It should be kept in mind, however, that homogenization step itself may cause contamination of samples by the materials for homogenization. Even a hard metal, such as stainless steel or titanium, could be scratched off and be contaminated into the homogenized samples during mechanical homogenization step. Fluoropolymers have been selected to prevent contamination by metals during homogenization, although fluoropolymers themselves may cause contamination by some organic materials including perfluorooctanoic acid (PFOA) and/or perfluorononanoic acid (PFNA).

Both glassware and plastic tubes have been used for sample storage vessels. They should be carefully pre-cleaned before sample storage. Although glassware is easier to clean organically and has been preferred for samples to be used for organic analysis, care should be taken to prevent break because volume of water (bloods, milk) increase substantially when frozen. Broken glass might cause injury and accidental infection when blood samples were stored. The vessels should be tightly capped. Metal screw cap or other loose cap might cause spill of liquid samples before freezing and desiccation of biological tissues during long-term storage under -20°C or higher. In the case of glass tube, plastic caps with inner elastomer covered with PTFE or other fluoropolymer is commercially available. Although fluoropolymer is chemically stable and durable, it contains perfluorinated chemicals, typically PFOA or PFNA, and this type of cap is not suitable for their analysis. A plastic cap tightly sealed without inner elastomer is preferred. Alternatively thin foil made of aluminum is sometimes used to cover the bottle mouth to prevent direct contact between the samples and inner elastomer of

the cap. It should be pointed out that aluminum foil is not organic contaminants free; its surface is apparently coated with some organic materials and sometimes low levels of target chemicals, including fluorinated chemicals, are detected. Baking foils together with glassware will be effective to minimize contamination levels. Extracts (organic solvents) from filters or other adsorbents should be kept in pre-cleaned, amber glass ampule sealed with inert gas, such as nitrogen or argon. Filters or other adsorbents will be covered with baked aluminum foil, be put into a zipped plastic bag (usually thin polyethylene bag), and be archived preferably in a freezer for future organic analysis. It is recommended to archive blank (unused) filters together with samples in order to check the occurrence of contamination within the material / during the storage.

Information on the distribution / localization of pollutants or their effects within the sample will be lost when homogenized. Some samples with annual ring or layered structure, such as sediment and coral cores, or with complicated structures like organisms or tissues, are preferably stored as a whole or separated into parts because homogenization step may cause loss of valuable information, such as temporal trends recorded in cores or expression status of specific genes in target organ.

8.3.3 QA/QC and security

There are two different levels of QA/QC procedures in the Environmental Specimen Banking; *i.e.*, 1) to check proper operation of the entire process, including sampling, sample handling and storage, according to the SOPs, and, 2) to check the sample quality (chemical composition) by the periodical analysis of the stored samples. Samples should be stored in areas where the access is limited to particular staffs. Regular training of staffs for not only regular operation but also for fire or other accidental situation is recommended.

Human samples may need special attention because of ethical issues and also danger of accidental infection. Special caution has to be paid to secure personal information (including questionnaires, genetic information and DNA itself). Usually “anonymizing” procedure is needed, *i.e.*, all the personal information belonging to the samples should be deleted, or be isolated from each sample. In the latter case, only a limited staff with special training and permission could access to the personal information separately stored under secure condition, and could link personal information to the individual sample (and obtained data from the sample) under permission of a special committee on ethical issues established under some authority. Pooled human samples, *i.e.* mixture of same amount of samples obtained from a group of people, are generally considered as “anonymous”.

8.4 Communicating Results to Decision-makers, Science and Public

Against the background of the high value of Environmental Specimen Banking for decision-makers and science, it is important to provide results of the activities in a timely and convenient manner. It is therefore recommended to establish an information system which allows to bring the concept of the banking into the policy arena and to inform the scientific community and interested public as well as the scientific community about its goals, topics, and especially about the results of the routine operation and its retrospective analyses of pollution trends. As an example, the German Environmental Specimen Bank provides their complete set of data resulting from the routine work on environmental and human specimens and retrospective analyses is compiled, edited, administered and published via the ESB Information System (www.umweltprobenbank.de).

8.5 Available Information on Environmental Specimen Banking

There are several major Environmental Specimen Bank facilities actively collecting samples in the world. Many of them have been operating in developed / industrialized countries, but interests in the bank have been increasing recently in developing countries, too (Becker et al., 2006; Becker and Wise 2010; Isobe et al., 2010).

Each bank has its own purpose and specific character, and has a different size and history. Variety of their experiences will be useful for setting up a new bank in a country / region where no Environmental Specimen Bank-related activities have been present. The information on their activities is available in scientific literatures (see, for example, references cited in Becker et al., 2006, which includes publications on the previous scientific meetings on the environmental specimen banking), and also their homepages. A website for the information exchange and research communication on the Environmental Specimen Banking is opened and maintained by German Federal Environment

Agency. SOPs of both German and US banks are available from the following homepage, together with list of homepages of major Environmental Specimen Banks in the world.

International Environmental Specimen Banking Group Homepage:

<http://www.inter-esb.org/>

Much larger activity is now present in life science / medical / livestock field to preserve human or other biological samples for medical / pharmaceutical / stock breeding purposes, and the term “biobank” has frequently been used as a repository for the purpose. As mentioned earlier, ISBER (International Society for Biological and Environmental Repositories) is an international society working on the technical, legal, ethical, and managerial issues relevant to repositories of biological and environmental specimens. ISBER fosters collaborations, creates education and training opportunities, and provides an international showcase for state-of-the art policies, processes, and research findings, and innovative technologies, products, and services on a global scale. In addition, ISBER has a both a regional chapter, ESBB (European, Middle Eastern and African Society for Biopreservation and Biobanking), which include members in these regions as well as an Affiliate Partner in Asia, the Asian Network of Research Resource Centers (ANRRC).

ISBER: <http://www.isber.org/>

ESBB: <http://www.esbb.org/index.html>

Information regarding construction and operation of the repository as well as existing candidate banks for the Convention may be found in these activities. In addition, many large hospitals in the world usually have emergency power generators and freezers. Regarding human samples, setting up a couple of freezers in such a large hospital or existing biobank facility having emergency power supply will be a cost-effective and feasible way to start banking under the Convention. As for environmental samples, use of commercial large scale refrigerated warehouses will be an alternative choice. As described above, however, the long-term operation of Environmental Specimen Banking will need special knowledge and techniques on the chemical analysis. It is indispensable to set up a close link between the operation of Environmental Specimen Bank and long-term monitoring programme or QA/QC activity under the GMP of the Stockholm Convention.

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ANNEX 1

Description of important parameters for the determination of POPs in air, human blood and breast milk

The following section is, to a large extent, taken from the recommendations for POPs analysis developed under the UNEP/GEF project “Assessment of Existing Capacity and Capacity Building Needs to Analyse POPs in Developing Countries”.

Before the start of any POPs analysis, an adequate study design has to be established to ensure that the sampling and subsequent analysis will meet the objectives of the study. All activities should be conducted by trained professionals, according to a well-designed plan and using internationally or nationally approved methods, carrying out the same method each time over the time span of the programme. It should be understood that mistakes in sampling or analysis as well as reporting or storage of data or any deviation from standard operational procedures can result in meaningless data or even programme-damaging data. Before initiation, the study design has to be discussed between and approved by all involved actors including the data users.

Laboratories may adopt published methods for sample extraction, clean up, and analysis, and have to validate them within the laboratory. The most basic requirements are:

- The laboratory must be able to prove competence for infrastructure, instrumentation, and well-trained staff to conduct specific analyses;
- Validation of the analytical methods including in-house methods;
- Standard operating procedures (SOPs) for the validated methods, including all the laboratory equipment and consumables;
- Quality criteria for quality assurance and quality control (QA/QC) described in the SOPs, *e.g.*, analysis of blank samples, use of reference materials, signal/noise ratio, and sensitivity of the analytical system.

Sampling

The aim of any sampling activity is to obtain a sample that can serve the objective of the study. In this activity it is considered indispensable to ensure the representativeness and integrity of the sample during the entire sampling process. Additionally, quality requirements in terms of equipment, transportation, standardization, and traceability are indispensable. It is important that all sampling procedures are agreed upon and documented before starting a sampling campaign.

Although it may be too expensive to get full accreditation for sampling, quality assurance and quality control (QA/QC) procedures for sampling should be put in place.

General sampling procedures

General sampling procedures include:

- Preparation of sampling equipment(s), eventually shipment of samplers;
- Establishment of criteria for acceptance of samples at the laboratory;
- Establishment of standard operation procedures for sampling;
- Establishment of quality assurance procedures, *e.g.*, field blanks, chain-of-custody;
- Establishment of field blank procedures.

Infrastructure and set-up

With respect to sampling indispensable requirements include:

- Equipment: Adequate sampling instruments according to the type of matrix and POP;

- Materials: Sampling instrumentation that is analyte-compatible, including utensils, containers, etc. (stainless steel-glass, never plastic);
- Personal protection: Those in charge of the sampling must wear adequate protection outfits depending on the type of samples they will work;
- Sample blanks: These allow for the assessment of potential contamination;
- Preservation: Samples and sample blanks are preserved according to matrix and type of POP requirements;
- Transportation: Adequate transportation that minimizes the possibility to contaminate the sample, ensuring its integrity and conservation until it reaches the laboratory in charge of the analysis;
- Availability of “in situ” monitoring equipment: To measure relevant environmental parameters according to each environment. The environmental conditions should be registered;
- Geo-referencing and photographic registers: Availability of GPS to locate sampling sites with precision and ensure future location of the site;
- Standardized protocol: Well-established sampling procedures have to be applied. Such sampling protocols have been developed by institutions or organizations such as ASTM (American Society for Testing and Materials), EC (European Commission), US-EPA (Environmental Protection Agency), GEMS (Global Environment Monitoring System), and WHO (World Health Organization);
- Labelling: Unambiguous labels are needed;
- Interview protocol: May be needed for human samples;
- Approval from an ethical committee: May be needed for human samples;
- Interface between sampling personnel and analytical laboratory: Close cooperation is crucial between project planners, the samplers, the analytical laboratory, and data users;
- Training of personnel: Personnel should be sufficiently trained and familiarized with the sampling techniques;
- Storage capacity: The laboratory must have an adequate storage capacity, *i.e.*, refrigerators or freezers at sufficiently low and stable temperatures, to ensure the integrity of the samples. These temperatures should be monitored constantly and documented;
- Waste Treatment: Consideration of suitable treatment/handling of the waste generated during the sampling.

Standard operating procedure (SOP)

A standard operating procedure (SOP) has to be established for each type of matrix. In these SOPs the following requirements must be addressed:

- The objective of the sampling exercise, including sampling protocols and specifications;
- Sample size in accordance with the analytical requirements and limitations in order to meet regulations or other objectives as given in the study;
- Description and geographic location of the sampling sites, preferentially with GPS coordinates;
- Guidelines for representative samples;
- Criteria for composite samples, *e.g.*, number of sub-samples, homogenization;
- Description of field blank procedures;

- Date, time of the sample taking;
- Conditions during sampling;
- Time intervals between sampling exercises;
- Specifications for the sampling equipment, including the operating, maintenance, and cleaning procedures (glassware can be cleaned by heating the glass to 300 °C over night);
- Identity of the person(s) who has taken the sample;
- Full description of sample characteristics;
- Labeling (sample numbers should be assigned in the protocol and prepared labels taken into the field);
- Labeling of samples (in the field) and sample registration for further follow-up;
- Indication of expected level of POP concentration in the sample;
- Any additional observation that may assist in the interpretation of the results;
- Quality assurance procedures to prevent cross-contamination.

The SOP should also contain a section with details on personal protective equipment that must be worn and listing of other safety concerns as appropriate.

Sub-contracting a sampling laboratory

No general recommendation can be given with respect to who should perform the sampling. For certain matrices, *e.g.*, human blood, a specialist, *i.e.*, medical doctor or nurse, has to take the sample. There are pros and cons for sub-contracting a laboratory specialist in sample taking. Sub-contracting the sampling can be an advantage to the laboratories that don't have the required personnel and equipment, but the laboratory must be sure that the sampling was taken established quality assurance and quality control (QA/QC) conditions.

In case a laboratory is sub-contracted to take the sample, it is recommended that the analytical laboratory establishes and provides the sampling protocol. Those in charge of the sampling process must apply security seals, as well as follow the preservation criteria to guarantee the integrity of the sample during transportation.

Transport and storage

The SOP also includes the requirements for transport and storage. More specifically, these are:

- Transport and storage conditions for each sample matrix including adequate facilities and infrastructure to be provided, *e.g.*, freezers;
- Preservation of integrity of samples during transport (temperature, light, etc.);
- Provisions for adequate storage, including:
 - Registry of the performance of refrigerators and freezers, *e.g.*, registration and control of temperature;
 - Availability of automatic power-supply equipment in case of power cuts;
 - There may be limits in storage times, temperature and other conditions;
- Preservation of individual samples for their re-analysis (counter-sample);
- Pre-analytical treatment of the sample: statistical criteria to obtain sub-samples and composite samples (pools) that are representative; homogenization of solids and tissue.

Note: there may be requirements for shipment to be addressed and respected. Especially in the case of international shipment, considerations for transport and customs' clearance must be taken into account since restrictions may exist.

Analysis

Key steps to be considered are:

- Procedures and acceptance criteria for handling and preparation of the sample in the laboratory;
- Standard QA/QC procedures must be followed by the laboratory;
- Participation at international intercalibration studies, analysis of certified or laboratory reference materials are essential.

Set-up and infrastructure [FORMAT: move to next page]

In order to guarantee preservation of the samples, control of potential cross-contamination, standardization of the technique, calibration, and good maintenance of instruments, the requirements listed below are considered indispensable. In general, the laboratory should be clean and safe, well organized, and have adequately trained staff to conduct the analysis. Having implemented the above mentioned measures may allow for accreditation. The requirements include:

- General laboratory environmental conditions should ensure enough laboratory space for each step of the analysis and avoid interference between individual samples. This includes:
 - Physical separation of standards and samples;
 - Expected POP concentration (minimize cross-contamination by separating highly contaminated samples from low contamination samples);
 - Control of temperature and provision of air-conditioning;
 - Availability of extraction hoods;
 - Handling area of inflammable products;
 - Provisions for laboratory waste disposal.
- Ensure and document the custody chain of the sample: verify the integrity and preservation of the samples (maintenance) in terms of temperature, containers, labels, registry, those responsible at each stage, establishment of acceptance criteria (conditions as well as quantity of material, according to analyte and matrix);
- Separation of aliquots: In the case of complementary analysis (for example, fat determinations) prior to the freezing of the sample;
- Selection and validation of the analytical method: Use method validation protocol according to the type of analyte and matrix (selectivity, repeatability, ability to reproduce, extraction efficiency, recovery, detection limit, quantification limit, accuracy). Quality of solvents and reagents (blanks). Clean glass material (avoid cross-contamination). Maintenance and calibration of auxiliary equipment (stoves, scales, test tubes, pipettes, glassware). Protocols and procedures must be clearly described and documented.

Extraction

There are various methods for extraction, which include Soxhlet, solid phase, liquid-liquid, and pressurized extractions. After extraction, the extract will be concentrated. In order to do so, the technique should be optimized to avoid excessive loss of the analyte. Typically, this step includes: evaporation under vacuum or with nitrogen (Note: control of temperature, flow of nitrogen, and vacuum are essential). Complete drying of the extract should be avoided; the possibility of adding a high boiling compound as a "keeper" may be considered.

- Before or during extraction, water, lipids, proteins, and sulfur should be eliminated. This can be done by:
 - Elimination of water by drying of the sample with sodium sulphate or equivalent demonstrated acceptable drying procedure;
 - Elimination of lipids with sulphuric acid or permeation in gels after extraction;
 - Denaturation of proteins with oxalate;
 - Elimination of sulphur with activated copper or by gel permeation after extraction.
- Purity of extraction solvents is also a major consideration. Only high purity glass distilled solvents should be used;
- Extraction should be standardized with respect to extraction times, type of solvent, and performance of auxiliary equipment;
- Before extraction, internal standards should be added to control the extraction efficiency;
- The recoveries of the extraction standards differ with POP to be analyzed and matrix. Based on current experiences (from international calibration studies) as a general rule:
 - For PCB and pesticides: 80 %-120 % (for tetra- and penta-chlorinated PCB recoveries down to 60 % can be accepted);
 - For PCDD/PCDF: 50 %-130 % (for hepta- and octa-chlorinated PCDD/PCDF 40 %-150 % can be accepted).

The extracts not used in the analysis can be stored, preferably in glass ampoules, at 20°C.

Clean-up

Clean-up is done to remove interfering substances/materials from the analyte in order to obtain unambiguous results. Purification should be efficient enough so that the chromatographic retention is not influenced by the matrix (especially when no labelled internal standards are used or no mass-specific detector is available).

Clean-up is performed with various combinations of adsorbents and solvents depending on selectivity, conditioning and column flow. During purification the following aspects need to be controlled or maintained:

- An internal standard is added at a concentration giving a signal/noise ratio of at least 20/1, with fixed concentrations of internal standards from sample to sample in order to obtain adequate response factors;
- Control fraction cut.

Separation

Separation of POPs is conducted using gas chromatography with electronic capture detector (ECD), mass selective detector (MS detector) or, if available, high-resolution mass spectrometry (HRMS). Other separation techniques, such as high pressure liquid chromatography (HPLC), have not been found adequate.

- In general, an appropriate stationary phase has to be selected and enough peak separation must be achieved to allow accurate quantification (general numeric criteria cannot be given, but the use of capillary columns with lengths of 30-60 m, internal diameters of 0.15-0.25 mm, a film thickness of 0.1-0.3 μ m and helium or hydrogen as a carrier gas should ensure sufficient resolution) (note: hydrogen cannot be used together with MS detection);
- Separation of critical pairs of compounds has to be verified, *e.g.*, pairs of PCB 28 and 31, 118 and 149; in dioxin analysis separation of PCDD/PCDF from polychlorinated diphenyl ethers (PCDE) should be checked;

- Helium, compared to nitrogen, gives a better choice to achieve the desired separation of pesticide POPs and PCB. The best carrier gas to achieve the required separation is hydrogen but it has some safety risk. If all the precautions and safety procedures are in place a hydrogen generator may be considered;
- Sample clean-up procedures should be efficient to prevent contamination of the detector;
- For PCB analysis and ECD detection, a minimum of two internal standards - one eluting at the beginning and one at the end of the chromatogram – should be used. It is recommended to also use one PCB congener that elutes in the middle of the chromatogram. Thus, the following three congeners are recommended: PCB #112, #155, and #198. These three congeners are quite stable and typically not found in commercial PCB mixtures. Note: decachlorobiphenyl (PCB #209) is not recommended because it tends to precipitate easily in standard solutions and due to long retention times, the peaks tend to be broad and have tailings. PCB #209 has also been identified in environmental samples and could not be quantified if this congener is selected as an internal standard;
- Adequate handling and preservation of all standards and reference materials;

Injection:

- Ensure cleanliness of injector (deactivated glass insert, evaluate activity with an acceptance criterion, for example, for DDE/DDT < 20 %);
- Verify the split/splitless relation, flows and state of septum;
- Repeatability must be ensured (for example, criterion < 5 %), and
- Verification of chromatographic conditions include:
 - Resolution, symmetric peak shape;
 - Reproducibility of retention times;
 - Purity of gases;
 - Use of second column of different polarity as confirmation column;
 - Verification of the linear range of the instrument.
 - Registration and traceability of services and performance of equipment.

Identification

The information available to identify the compounds eluted from the gas chromatographic column depends on the type of detector being used. The following criteria may generally be used:

- Retention time should match between sample and internal standard;
- Confirmation of peaks can be performed on a second column with different polarity;
- Matrix spikes (or co-injection) are recommended to verify components and check the quantification;

For HRGC-ECD combinations, the following specific recommendations are given:

- Retention time \pm 0.2 min;

For HRGC-MS detection combinations, the following specific recommendations are given:

- Positive identification should be done on isotopic ratios within 20 % of theoretical value;
- For positive identification with MS detection, the retention time of the labelled internal standard to the native compound should be within 3 seconds;

- The use of MS libraries is useful (if full scan).

Quantification

In general, quantification of the analyte should be done according to the internal standard methodology. For PCDD/PCDF and dioxin-like PCB, typically additional requirements are needed. The following requirements are considered to be indispensable:

- At least one standard representative for the POPs analyte group analyzed should be added at the normal level of quantification;
- For quantification it must be assured that the concentration of the compounds is within the previously determined linear range of the detector (Note: Not necessary when multi-level calibration is performed!);
- Integration: select the baseline level and the adequate signal to noise relation of integration according to the type of sample, verify the general form of the chromatogram, the form of the peaks and manually verify integration;
- Verification that the concentration of blanks is significantly lower than the samples; recommendation: < 10% ;
- Noise should be defined as close as possible to the peak of interest;
- At least 10 data-points should be sampled across a peak for quantification (Note: some instruments do so automatically);

Calibration:

- Labelled internal standards are an added value;
- Multi-point calibrations should be carried out;
- Daily calibration checks in connection with analyzing a series of samples should be done (for large batches calibration drifts have to be checked during the run);
- Suitable laboratory reference material should be used to verify the performance.

Reporting

Data compilation and reporting together with data storage are the final steps in analysis. The report form must include:

- Date, name of the sample and description, method used, the name of staff that has performed analysis, and signature of person in charge of the POPs laboratory;
- Only SI units (International System) should be used and should be verified before clearing the report;
- Clear references to the basis for the concentration must be given, *e.g.*, fresh weight, lipid weight, or volume;
- Data below the LOQ but above the LOD should be reported as "LOD-LOQ", data below LOD as "<LOD";
- Recovery efficiency should be reported;
- Measured or estimated information on the uncertainty in the results should be made available;
- Reporting values should not be corrected for percentage of recovery;
- It should be demonstrated that the blank is 10-times lower than the value that is reported. Reporting values should not be corrected by laboratory blanks (Note: There may be high fluctuations for laboratories' blanks, *e.g.*, for PCB 118). Handling of all blanks needs written

documentation; in the case of high laboratory blanks; handling of such cases and justification should be clearly indicated in the SOP;

Definitions

Limit of detection and limit of quantification are defined as follows:

- LOD should be 3 times the noise;
- LOQ should be 3 times the LOD.

Results for sum parameters where one or several individual compounds are <LOQ should be reported as intervals with a lower bound limit calculated with the <LOQ set to 0, and the upper bound limit with <LOQ set equal to LOQ.

There are two methods available to provide information on uncertainty:

- Quantification of uncertainty for each step;
- Overall uncertainty derived from inter- and intra-laboratory results.

Further important issues to consider:

Maintenance of equipment

The maintenance of the analytical equipment is considered as one of the most important aspects in POPs analysis. It is very expensive to have service contracts for all the maintenance and therefore it is important to train the laboratory personnel to do the basic maintenance when the QA/QC results are unacceptable.

Laboratories must arrange for proper training, including basic maintenance, when new equipment is installed in the laboratories.

Training of laboratory staff

Human resources are crucial for any analytical work. The following specific problems need to be addressed and resolved:

The lack of skilled laboratory personnel to conduct the analytical work has been identified as one of the critical problems;

The training requirements. Two levels of training exist:

- Training of people to follow the analytical procedures and to report the results;
- Training of people to do troubleshooting and conduct the necessary maintenance when the QA/QC criteria fail;
- Countries with experienced personnel should assist other countries with training of laboratory personnel;
- There is a need in the region for training courses and annual training workshops for the transfer of technology know-how.

Housing

For POPs analytical laboratories there are certain requirements as to housing. These include:

- Proper environmental conditions (humidity is a most critical factor) for instrumental analysis but also for sample preparation;
- Minimization of vibration (most important for HRMS instruments);
- Temperature control for helium carrier gas used with ECD;
- At certain locations where the incoming air has to be cleaned. Ideally this would involve a well ventilated lab with air pre-filtered through HEPA (HEPA Corporation) and carbon filters. The analysis of blank samples will disclose background interferences, and to identify the influence

from the laboratory environment, a small volume of a solvent left in an open Petri dish for a couple of days will catch the compounds in the atmosphere;

- Occupational Health Safety venting;
- Environmentally sound/safe disposal of laboratory wastes and highly contaminated samples must be guaranteed.

References

UNEP/GEF POPs Laboratory Project: <http://www.chem.unep.ch/pops/laboratory/default.htm>

The full text of the guidelines can be downloaded from:
<http://www.chem.unep.ch/pops/laboratory/documents.htm>

ANNEX 2

Possible structure of environmental long-range transport reports

It has been noted that the Global Report of the Regionally Based Assessment of Persistent Toxic Substances (GEF/UNEP 2000/3) included an assessment of knowledge on the long-range transport of these substances. The structure used in that study is considered to have functioned well and it is suggested that it could provide a first draft structure for a single transport report to serve both regional and global transportation elements as required under Article 16. This structure is provided here without modification to assist in planning and in the preparation of a report structure.

- 1 The reason for interest in environmental transportation pathways**
- 2 Comparison of the substances in annexes a, b and c for environmental transportation pathways**
- 3 Comparison of pops environmental transport behaviour in the regions**
 - 3.1 Region specific influences on atmospheric transport of persistent organic pollutants**
 - 3.1.1 Influence of airflow patterns on atmospheric transport of persistent organic pollutants**
 - 3.1.2 Influence of air-surface exchange and degradation on atmospheric transport of persistent organic pollutants**
 - Atmospheric degradation
 - Atmospheric deposition
 - Low latitudes
 - Mid-latitudes
 - High-latitudes
 - 3.2 Region-specific environmental transport**
 - Influence of currents on oceanic transport
 - Influence of particle settling and degradation on oceanic transport
 - 3.3 Region-specific influences on riverine transport**
 - 3.4 Region-specific influences on transport by migratory animals**
- 4 POPs environmental fate and transport**
 - 4.1 Generic approaches to long-range environmental transport potential assessment**
 - 4.2 Regional approaches to long-range environmental transport potential assessment**
 - Spatially unresolved regional box models
 - Spatially resolved regional box models
 - Highly resolved meteorology-based regional transport models
 - 4.3 Global approaches to long-range environmental transport potential assessment**
 - Spatially resolved global box models
 - Highly resolved meteorology-based global environmental transport models
- 5 Uncertainties**
- 6 Summary**

ANNEX 3

Sampling, storage, transportation, and analytical details for maternal blood (source: Centre de toxicologie du Québec / INSPQ).

Sampling protocol for the determination of organochlorinated pesticides, PCBs and PBDEs in blood

Material

Tube (2 x 6 mL or 1 X 10 mL) of blood on EDTA as anticoagulant (lavender top).

Sampling

- For each patient, draw a 10 mL sample on a lavender-top Vacutainer (EDTA, Becton-Dickinson).
- Immediately invert the tube 7 to 8 times to mix the anticoagulant.
- Cool slowly to 4°C (do not place directly on ice to avoid hemolyzing the sample)
- Centrifuge 10 minutes in order to separate the plasma from the red blood cells.
- Transfer the plasma using a polyethylene pipet (Baxter # P5214-10) into a 7ml screw cap precleaned glass vial sealed with a Teflon disc. (Supelco # 2-7341).

Storage

If samples are sent to the laboratory within 5 days :

Keep at 4 °C until shipped.

If samples are kept for more than 5 days :

Keep at – 20 °C until shipped.

The plasma sample will not deteriorate for at least five days at room temperature. Therefore, even if the samples were to reach room temperature during transportation, no deterioration should occur.

Shipping

Tubes should be wrapped separately and placed in a shock-resistant container. In order to avoid transportation delays which could affect sample integrity, it is recommended to use courier services (eg FedEx) for rapid delivery. Please email us the courier tracking number (at ctqlab@inspq.qc.ca)

Send samples early in the week to the following address:

Laboratoire de la toxicologie

Centre de toxicologie / INSPQ

945 avenue Wolfe

4ème étage

Québec, QC

G1V 5B3

Phone : (418) 650-5115 ext 5100

Analytical method for the determination of polychlorinated biphenyl congeners, polybrominated congeners, toxaphenes congeners and organochlorinated pesticides in plasma by GC-MS (E-446) -condensed version-

Type of method

Solid phase extraction followed by gas chromatography coupled to mass detection

Application range

Analyte(s)	From/To (µg/L)
Aldrin	0,024 to 10
Aroclor 1260	0,127 to 100
PCB 28	0,074 to 10
PCB 52	0,928 to 10
PCB 99	0,089 to 10
PCB 101	0,024 to 10
PCB 105	0,0050 to 10
PCB 118	0,012 to 10
PCB 128	0,0050 to 10
PCB 138	0,016 to 10
PCB 153	0,011 to 10
PCB 156	0,0050 to 10
PCB 163	0,0090 to 10
PCB 170	0,0060 to 10
PCB 180	0,0070 to 10
PCB 183	0,0050 to 10
PCB 187	0,0040 to 10
α-chlordane	0,0050 to 10
γ-chlordane	0,0030 to 10
β-HCH	0,018 to 10
cis-nonachlore	0,0050 to 10
p,p'-DDE	0,294 to 50
p,p'-DDT	0,035 to 10
Hexachlorobenzene	0,018 to 10
Mirex	0,025 to 10

Oxychlordane	0,007 to 10
PBB 153	0,030 to 10
PBDE 47	0,095 to 10
PBDE 99	0,042 to 10
PBDE 100	0,052 to 10
PBDE 153	0,030 to 10
Parlar 26	0,0060 to 2,0
Parlar 50	0,0040 to 2,0
Trans-nonachlore	0,0080 to 10

Instrumentation

Chromatograph # 6890 (Agilent) with ECD detector (Agilent G2397A) and mass detector (Agilent 5973 Network)

Description

Plasma samples are enriched with internal standards and denaturated with formic acid. Organohalogenated compounds are automatically extracted from the aqueous matrix using solid phase separation. Extracts are cleaned up on florisil columns to be analysed by GC-MS. Ions generated are measured after negative chemical ionization. Analyte concentrations are evaluated by considering the % recovery of labelled internal standards. The ECD detector serves to verify the detection limits for PCB congeners 28 and 52.

Detection limit and precision

Analyte(s)	Detection limit (µg/L)	Reproducibility (%)
Aldrin	0,0070	Non available
Aroclor 1260	0,038	7,3
PCB 28	0,022	13,3
PCB 52	0,279	11,0
PCB 99	0,027	8,0
PCB 101	0,0070	9,7
PCB 105	0,0020	7,4
PCB 118	0,0040	7,7
PCB 128	0,0020	Non available
PCB 138	0,0050	8,6
PCB 153	0,0030	7,5
PCB 156	0,0010	9,7
PCB 163	0,0030	8,0
PCB 170	0,0020	10,4
PCB 180	0,0020	8,4
PCB 183	0,0020	,3

PCB 187	0,0010	8,4
α -chlordane	0,0020	Non available
γ -chlordane	0,0010	Non available
β -HCH	0,0050	11,4
cis-nonachlore	0,0010	11,4
p,p'-DDE	0,088	12,7
p,p'-DDT	0,010	16,9
Hexachlorobenzene	0,0050	8,9
Mirex	0,0080	12,2
Oxychlordane	0,002	14,7
PBB 153	0,0090	25,2
PBDE 47	0,028	20,6
PBDE 99	0,013	23,3
PBDE 100	0,015	18,0
PBDE 153	0,0090	35,9
Parlar 26	0,0020	6,9
Parlar 50	0,0010	6,2
Trans-nonachlore	0,0030	11,2

ANNEX 4

Fourth WHO-Coordinated Survey of Human Milk for Persistent Organic Pollutants in Cooperation with UNEP (electronic only)

(the text is provided in a separate document and is to be included in the hard copy)

ANNEX 5

Standard operation procedures and protocols for air monitoring (electronic only)

(the text is provided in a separate document and is to be included in the hard copy)

ANNEX 6

Water solubility, octanol-water, and organic carbon partitioning coefficients of POPs

Listed Chemical	Representative Analyte in water	Water solubility ¹ (mg/L) at 25°C	Log Kow	Log Koc ²	Ref ³
Aldrin	Aldrin	0.02	3.0	2.6	1
Chlordane	<i>cis</i> -(\square)chlordane	0.056	6.0	5.5	1
Chlordecone	Chlordecone	2.7	4.5	3.4	2
DDT	4,4'-DDT	0.0055	6.2	5.4	1
	4,4'-DDE	0.04	5.7	5.0	1
Dieldrin	Dieldrin	0.17	5.2	4.1	1
Endrin	Endrin	0.23	5.2	4.0	1
Endosulfan	α -Endosulfan	0.5	4.9	3.6	2,3
	Endosulfan sulfate	0.22	3.6	3.2	2,3
HCB	HCB	0.005	5.5	5.0	1
Pentachlorobenzene	PeCBz	0.65	5.0	4.5	1
Heptachlor	Heptachlor epoxide	0.35	5.0	4.0	1
Hexabromobiphenyl	HBB	0.011	6.4	5.9	4
Hexachlorocyclohexanes	\square -HCH	1.0	3.8	3.8	1
	\square -HCH	7.3	3.7	3.0	1
Mirex	Mirex	6.5×10^{-5}	6.9	6.0	1
Perfluorooctane sulfonate (PFOS)	PFOS	680	-	2.6	5,6
Polychlorinated biphenyls (PCB)	PCB 28	0.16	5.8	5.3	1
	PCB 52	0.03	6.1	5.6	1
	PCB 101	0.01	6.4	5.9	1
	PCB 153	0.001	6.9	6.4	1
Polychlorinated dibenzo- <i>p</i> -dioxins (PCDD)	TCDD	1.93×10^{-5}	6.8	6.3	1
Polychlorinated dibenzofurans (PCDF)	TCDF	4.19×10^{-4}	6.5	6.0	1
Toxaphene	P26	-	5.5	5.0	7
	P50	-	5.8	5.3	7
Pentabromo diphenyl ethers	BDE 47	0.011	6.8	6.3	8,9
	BDE 99	0.0024	7.3	6.8	8,9
Octabromo diphenyl ethers	BDE 183	-	8.3	7.8	9

¹Water solubility of the solid and reported in mg/L

²Koc estimated from Seth et al (1999)

³References cited in Section 4.2.1.: 1. Mackay et al (2006); 2 ATSDR (2000); 3. Weber et al. (1997); 4 USEPA (2008); 5 UNEP (2006); 6 Higgins and Luthy (2006); 7 Muir et al (2006); 8 European Commission (2001); 9 Braekvelt et al. (2003). Full references cited in Section 4.2.1.

ANNEX 7

Water Monitoring Programmes targeting PTS based on a survey of the UNEP PTS reports **REGIONAL AND NATIONAL MONITORING PROGRAMMES**

ANTARCTICA

Japanese campaign

Surface water samples were collected from the Western Pacific, Eastern Indian and Antarctic Oceans from 1975 to 1985, as in the table below. Results are reported in the Persistent Toxic Substances Report for Central and North East Asia, in Tatsukawa et al (1990) and in other reports (Table A1).

Table A1. Details of samples collected during survey cruises between 1975 and 1985

Cruise no.	Date	Reference
1	May 1975	Tanabe et al 1982a
2	July-Aug 1976	Tanabe et al 1982a
3	Oct 1976 – Jan 1977	Tanabe et al 1982a
4	Jan-Feb 1978	Tanabe et al 1982a
5	June-July 1979	Tanabe et al 1982a
6	July 1979	Tanabe et al 1982a
7	Nov 1980 – Mar 1981	Tanabe et al 1982b
8	July 1982	Unpublished (Tanabe, Ehime University)
9	Dec 1982	Unpublished (Tanabe, Ehime University)
10	Nov 1983 – Jan 1984	Kwano et al 1985
11	Sept – Oct 1985	Unpublished (Tanabe, Ehime University)

At the regional scale the Council of Managers of National Antarctic Programmes (COMNAP) formed Antarctic Environmental Officers Network (AEON) to provide for harmonized monitoring in the Antarctic. A summary of existing monitoring activities from 15 countries was published by COMNAP in May 1998.

ARCTIC (AMAP report 2002)

Rivers

Sampling and analyses of POPs in Russian rivers during the period 1990-1996 were carried out by regional laboratories of ROSHYDROMET (Federal Service of Russia on Hydrometeorology and Environment). Sampling took place at stations along major Russian rivers that are tributaries to the Arctic Ocean. Most attention was focused on the stations located further downstream in each large river in order to estimate loadings to the Arctic Ocean.

More recently, a project was conducted in Russia in 2001-2002 to study contaminants in the Yenisey and Pechora rivers (RAIPON/AMAP/GEF Project, 2001). Samples of freshwater (15-45 L) were collected from lakes and rivers in four regions of the Russian Arctic: Kola Peninsula (Lake Lovozero); Pechora River mouth at Nelmin Nos; Taymir Peninsula (Yenisey River at Dudinka and Khatanga River at Khatanga), and at Kanchalan on the Kanchalan River in Chukotka, in 2000- 2001 for analysis of POPs. Samples from Lake Lovozero were collected at various depths (0 -30 m). There did not appear to be trends in OC concentrations with depth, and therefore, these data have been combined. Samples from all other sites were collected from rivers near the surface.

RAIPON/AMAP/GEF Project (2001). Persistent Toxic Substances (PTS), Food Security and Indigenous Peoples of the Russian North. V. Kimstach. Arctic Monitoring and Assessment Program Oslo, Norway.

Sea water

A large number of measurements of OC pesticides and PCBs have been made in Arctic Ocean waters in the period of 1996 to 2001 mainly as a result of scientific cruises organized by circumpolar countries. The measurements have, for the most part, been conducted from oceanographic research vessels in a series of cruises. The Swedish Oden cruise in 1996 conducted sampling from the ice edge to the North Pole in the northern Barents Sea. In 1997, a Canadian supply trip (JOIS) for the Surface Heat Budget of the Arctic (SHEBA) study (Perovich et al., 1999) was used to obtain seawater from the western Canadian Arctic Archipelago in September. In May-June 1998, the Northwater Polyna study in Northern Baffin Bay (NOW '98) provided another platform for sampling. In 1997-1998, the SHEBA study permitted continuous sampling of seawater over the Beaufort/Chukchi Seas. The Swedish Tundra Northwest study (TNW '99) traversed the Canadian Arctic Archipelago during July/August, 1999. An Arctic to Antarctic cruise by the RV Polarstern provided seawater samples from the East Greenland Sea in 2000. Studies have also been conducted in the Marginal Ice Zone of the Barents Sea north of Svalbard (Olsson, 2002) and in the Laptev Sea (Utschakowski, 1998).

Some investigators used filtration or continuous centrifugation to remove particles; samples for HCH analyses were often unfiltered. HCH isomers were the most commonly measured chemicals in the Arctic Ocean and adjacent seas. These compounds are present at ng/L concentrations and there are few problems with contamination on ships or in the laboratory. PCBs were the next most prominent contaminants; however, there were far fewer measurements. PCB measurements in seawater are challenging because of low levels and potential for shipboard as well as laboratory contamination. Comparison among different studies and with previous work on PCBs in Arctic and northern temperate seawaters (Iwata et al., 1993; Schultz-Bull et al., 1998; Sobek and Gustafsson, 2004) raises questions about contamination and the effects of different sampling techniques. These include possible differences between whole (unfiltered) water versus filtered samples, and the use of in situ collection using remotely deployed samplers versus submersible pumping onto the ship.

ASIA

In general, monitoring activities are systematically performed especially in the more developed countries. The Ministry of the Environment of Japan has been conducting surveys for nearly three decades to monitor environmental levels of certain POPs in different environmental compartments, including coastal water areas.

Some regional initiatives were also developed for monitoring coastal environment (coastal water as well as rivers and fresh water bodies close to the coastal areas), such as the one coordinated by the United Nations University (UNU). Under the Monitoring and Assessment Network for Asian Governance of Environment (MANAGE) (<http://www.unu.edu/esd/manage/index.html>), UNU has been implementing a capacity development project on chemical analysis of environmental pollutants since 1996 (Environmental Monitoring and Governance in the Asian Coastal Hydrosphere). Eight laboratories in different countries across this region have been undertaking regular monitoring activities, focusing on a range of recognized POPs. Participating laboratories are located in China, Indonesia, Korea, Malaysia, the Philippines, Singapore, Thailand and Vietnam. The results from the monitoring work in these countries have been collected by UNU to form a regional database on environmental pollution (Proceedings of the KJIST- UNU – UNESCO International Workshop on Regional Environmental Quality in the East Asian Coastal Hydrosphere, <http://landbase.hq.unu.edu/Publication/KwangjuProceedings.pdf>).

AUSTRALIA AND NEW ZEALAND

Ongoing monitoring programmes in the region include the National Dioxins Program (Australia) and the Organochlorines Program in New Zealand. The latest technical report on dioxins in aquatic environments in Australia can be found at <http://www.environment.gov.au/settlements/publications/chemicals/dioxins/report-6/index.html>.

Under New Zealand's Organochlorines Program, a series of investigations of the levels of organochlorines have been performed on several media, including estuaries and rivers (<http://www.mfe.govt.nz/issues/hazardous/contaminated/organochlorines.html>).

SOUTH AMERICA, AFRICA

No regional monitoring programmes are listed for the region.

CENTRAL AMERICA AND THE CARIBBEAN

Table 2 provides an overview of the sampling campaigns in Central America and the Caribbean and their results (UNEP 2002b).

Table A2. Levels of organochlorine pesticides and PCBs in water samples from marine environment.

Country/ year	Area	Results	Observations	Reference
Colombia 1996	Coastal ecosystems Ciénaga de la Virgen, Cartagena former rice fields	DDT 2.5 – 53.4 ng/g DDE <0.001- 0.5 ng/g DDD <0.001- 3.6 ng/g PCBs 0.1-173 ng/g		Castro, 1997
Honduras 1995-97	Pacific Ocean, Golfo de Fonseca 3 estuaries	Maximum concentrations: β -endosulfan 0.03 mg/L Lindane 0.02 mg/L p,p'-DDT 0.012 mg/L Heptachlor epoxide 0.01 mg/L Endrin 0.011 mg/L	Results indicate a widespread contamination of coastal waters. Most concentrations were low.	Meyer, 1999
Jamaica	Kingston Harbour	Mean levels: α -endosulfan 2.2 μ g/L β -endosulfan 7.86 μ g/L Endosulfan sulphate 0.003 μ g/L p,p'-DDT 7.02 μ g/L Dieldrin 1.88 μ g/L Endrin 0.26 μ g/L Lindane nd	Pesticides were also detected in sediments samples from the harbour. Contamination caused by discharge from the Rio Cobre, among others by the use of endosulfan 2-3 times/ year in coffee plantations.	Mansingh et al., 2000
Jamaica 1990-91	Portland, north east coastal waters	Mean levels α -endosulfan 0.42-7.12 μ g/L β -endosulfan & p,p'-DDE 0.8 μ g/L	Coffee production area. Pesticides detected also in sediment and biota.	Robinson & Mansingh, 1999
St Lucia 1986-89	Coastal sites	Maximum concentrations found Lindane 5-40 ng/L Dieldrin 4 ng/L DDT 4-20 ng/L		Magloire, 2002

MEDITERRANEAN

The MEDPOL Programme for the marine environment
(<http://195.97.36.231/medpol/index.asp?doc=general.htm>), issued from the Barcelona
Convention aims to:

- present periodical assessments of the state of the environment in hot spots and coastal areas (needed to provide information for decision makers on the basic environmental status of the areas which are under anthropogenic pressures);

- determine temporal trends of some selected contaminants in order to assess the effectiveness of actions and policy measures, and
- enhance the control of pollution by means of compliance to national/international regulatory limits.

Trend monitoring of loads aims to provide estimates of inputs of some major groups of pollutants, hazardous substances and nutrients listed in the Land Based-Sources Protocol to the coastal marine environment via point (rivers, municipal and industrial effluents) sources.

Participant countries include: Albania, Algeria, Croatia, Cyprus, Greece, Israel, Morocco, Slovenia, Syria, Tunisia and Turkey. Sea water monitoring activities started in 1996 and data is currently available until 2006, including levels of chlorinated biphenyl congeners, chlorinated pesticides, and organo-phosphoric pesticides.

EUROPE

Extensive sea water monitoring programmes exist (OSPAR, HELCOM); some are newer (Caspian Sea, Black Sea). As far as rivers, the monitoring is mainly realized at the

national level, but a lot of multinational or regional activities already exist (Rhine, Danube). The main regional rivers such as Elbe, Rhine or Danube and their main tributaries are frequently and regularly monitored.

The Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR Convention) was signed in 1992. In 1994 the OSPAR Commissions agreed to develop a new joint monitoring programme for the maritime area of the Oslo and Paris Conventions and to update the Joint Monitoring Programme of the Oslo and Paris Commissions and the Monitoring Master Plan of the North Sea Task Force. This joint monitoring programme is called the Joint Assessment and Monitoring Programme (JAMP). The region covered by the monitoring programme is the North-East Atlantic which, in turn, is divided in five regions: Arctic Waters (Region I), the Greater North Sea

(Region II), the Celtic Seas (Region III), the Bay of Biscay and Iberian Coast (Region IV) and the Wider Atlantic (Region V).

The core marine environmental monitoring activity under the JAMP is the OSPAR Coordinated Environmental Monitoring Programme (CEMP; http://www.ospar.org/content/content.asp?menu=00900301400000_000000_000000), which currently focuses on monitoring of the concentrations and effects of selected contaminants and nutrients in the marine environment as follows:

- metals (cadmium, mercury and lead) in sediment and biota
- PAHs in biota and sediment
- PCBs in biota and sediment
- brominated flame retardants in biota and sediment
- tributyltin in sediment and its effects in gastropods
- nutrients in sea water
- eutrophication effects

HELCOM is the governing body of the Convention on the Protection of the Marine Environment of the Baltic Sea Area. The Commission works to protect the marine environment of the Baltic Sea from all sources of pollution through intergovernmental co-operation between Denmark, Estonia, the European Community, Finland, Germany, Latvia, Lithuania, Poland, Russia and Sweden. HELCOM monitoring programmes in the Baltic provide regular information on the levels and trends of selected heavy metals and some organic pollutants. The guidelines for the compilation for waterborne pollution load to the Baltic Sea can be found at http://www.helcom.fi/groups/monas/en_GB/plcwaterguide/

As part of HELCOM monitoring initiatives, during 2008-2009 IVL and NILU have performed a screening study in the eastern Baltic Sea environment on the occurrence of eight substances / substance groups identified as hazardous under the Baltic Sea Action Plan. Of the eight substances included in the study, six of them were found above LOQ: organic tin compounds, PBDEs, PFAS, nonylphenol, chlorinated paraffins and endosulfan. PFAS (PFOS and PFOA), octylphenol and nonylphenol were found in one, one and six water samples respectively (<http://www3.ivl.se/rapporter/pdf/B1874.pdf>).

The Caspian Environment Programme (CEP; <http://www.caspianenvironment.org/newsite/index.htm>) is a regional programme developed for and by the five Caspian Littoral States, Azerbaijan, Iran, Kazakhstan, Russia and Turkmenistan. The Regional Environmental Monitoring Programme (REMP) for the Caspian Sea includes a marine physical and chemical monitoring component (water and sediment analysis). Key indicators include:

- Hydrocarbon contamination from refineries, ports and harbours and shipping
- Nutrient enrichment arising from sewage discharges, fertiliser production and agricultural run-off
- Pesticide contamination arising from spillage, large-scale pest control programmes and agricultural run-off

Similarly, the Black Sea Environment Programme (BSEP) equally includes a monitoring component of aquatic pollution along with capacity building in this area (http://www.iwlearn.net/iw-projects/Fsp_11279946709/project_doc/black-sea-environment-programme-project-final-summary-report-76p-776k.pdf).

INDIAN OCEAN

No systematic monitoring is specified for this region.

NORTH AMERICA

The US EPA Great Lakes National Program Office conducts monitoring programs that sample the water, aquatic life, sediments, and air in order to assess the health of the Great Lakes ecosystem (<http://www.epa.gov/glnpo/monitor.html>).

The Canadian Surface Water Monitoring and Assessment Programme includes three general components: River Systems Monitoring and Assessment, Great Lakes Near-shore Monitoring and Assessment, and Inland Lake Monitoring (<http://www.ene.gov.on.ca/envision/techdocs/3933-1.htm>).

PACIFIC ISLANDS

There is limited capacity for monitoring in the region. Existing national facilities are available only in some of the larger countries and some are owned by regional institutions. There are laboratories capable of testing in Fiji, Samoa, Tonga, New Caledonia, French Polynesia, and Guam.

Data is available from a large-scale Japanese study of Asia and Oceania which analyzed six water samples from Solomon Islands (1992)

MONITORING ACTIVITIES AT THE GLOBAL LEVEL

UNEP Global Environment Monitoring System GEMS

UNEP GEMS/Water (Global Environmental Monitoring System/Freshwater Quality Programme; <http://www.gemswater.org/>) has been working on a compilation of monitoring data for water. The GEMS/Water programme is a multi-faceted water science programme oriented towards understanding freshwater quality issues throughout the world. Major activities include monitoring, assessment, and capacity building. The implementation of the GEMS/Water programme involves several United Nations agencies active in the water sector as well as a number of organizations around the world.

Monitoring data for physical/chemical pollution parameters, major and minor ions and organic contaminants, including POPs are reported by 106 participating countries.

Table A3. Station and Parameter Classification within UNEP GEMS

Region	Number of Stations	Number of Data Points	Organic Contaminants	Date Range
Africa	138	206907	1732	1977 - 2007
Americas	662	417994	594344	1965 - 2006
Asia	332	641940	8646	1971 - 2007
Europe	318	823323	23985	1978 - 2005
Oceania	94	206650	1438	1979 - 2006
Total	1544	2296814	630145	1965 - 2007

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TECHNICAL NOTE

Technical Note to Chapter 3 Statistical Considerations

1. Introduction

The aim of this technical note is to complement the statistical methodology published in the GMP Guidance Document, and to specify methodical procedures which should be employed when processing POPs concentration data reported in the GMP reports. Based on the practical data processing experience with the first GMP reports, this technical note specifies obligatory data fields which should be filled in order to allow correct interpretation of the data analysis. Finally, this text highlights the most important data pre-processing and processing steps and proposes a logical sequence of the statistical outcomes. The methodology is based on robust statistical methods which can be generally applied for statistical analysis of POPs concentrations in any environmental matrix.

2. General principles

2.1 Data pre-processing

The correct definition of data is a prerequisite for the subsequent statistical analysis. Only reliably reported concentration values can be accepted for any spatial or temporal comparison. Therefore, a multilevel evaluation procedure based on the annually aggregated concentration values is proposed in order to maintain a high predictive value of the GMP records while avoiding bias in the concentration values.

The evaluation of the first GMP reports revealed a number of challenges related to data standardization, such as the lack of a standardized taxonomy for the listed POPs, their isomers, transformation products and summations. Some records provided detailed primary data, including rarely measured compounds, while others contained only the sums of the key groups of POPs. The heterogeneity of the data was further enhanced by reporting various toxic equivalents (TEQ) (based on the WHO TEF values from various years) rather than concentrations of the individual PCDDs, PCDFs and PCB congeners. Unclear identification of matrices, units, time scales of reported concentrations, as well as insufficient specification of aggregated data have also been identified. Large volumes of valuable data have been generated in all regions through the first GMP reports, and further standardization of reporting formats would significantly improve their applicability. A more elaborated guidance for handling, reporting and analyzing/interpreting these data will thus improve their applicability and support the development of the second GMP reports.

The practical experience with the processing and validation of GMP1 records serves to establish data handling rules for the future data collection campaigns. The rules define mandatory data fields which correspond to the standardized structure: typology of the background site; definition of the sampled matrix; taxonomy of parameters; sampling frequency (and data aggregation, if applied); measured value defined by its unit and variability.

The proposed data evaluation procedure guarantees comparability of the different samples, especially from the point of view of the type of site, matrix, sampling method, time span and sampling frequency. Heterogeneity in these factors might dramatically increase the uncertainty in the final outcomes. The pre-processing procedures also limit the impact of uncontrolled covariates and thus reduce the risk of false trend detection or neglecting truly significant changes.

- a) Initial data filtering stratifies the records according to the objective entities, such as site-matrix type and analyzed compounds. The filters must also check/verify the completeness of the primary database records in the reported sampling frequency, number of detected LOQs and their handling rules.
- b) In the statistical part, the validation procedure excludes obvious extreme or unreliable values from quantitative analyses. The outlying concentrations can be identified by checking their quantile position in the sample distribution function. Estimated mean and standard deviation of log transformed annually aggregated data can be used for the reconstruction of the normal or log-normal distribution; a resulting pattern can be used to assess probabilistic position of the point values.

2.2 From primary to aggregated POPs concentrations [FORMAT; MOVE TO NEXT PAGE]

The most important source of variability in the atmospheric concentrations of POPs is their seasonal dynamics. This is not the case for human tissue data. Provided that primary concentration data sets are available, the impact of seasonality can be quantified and extracted from the time series (proper smoothing techniques, adjusting statistical models). Seasonally-adjusted time series constitute a base for the subsequent trend detection and quantification.

Annually aggregated data can also be used for spatial and temporal comparisons and quantification of time-related trends. In the first GMP reports, most records are annually aggregated arithmetic means. Nevertheless, the aggregated values must be reported with appropriate variability estimates generated from primary data (5th-95th percentile range and standard deviation are recommended). The quantity of non-detects (below LOQ values) in the primary records and their handling in the mean calculations must be reported as well.

2.3 Statistical testing and its power

Power analysis is an obligatory step to define the magnitude of changes reliably detectable by the statistical methods. Power analysis minimizes the risk of misinterpretation or incorrect generalization of the observed values. The power calculation must be applied for both the statistical trend detection (Mann-Kendall algorithms) and quantification (paired tests assessing the difference in the annual arithmetic or geometric means). Two approaches are recommended for GMP data testing, especially for the time trend detection:

- a) Quantification of the minimum detectable difference between the annually aggregated values allowing to benchmark the identified changes against the statistically detectable levels;
- b) Prospective calculation of the sample size needed for the detection of a given relative time change in the POPs concentrations (e.g. 50% annual decrease).

2.4 Exploratory and confirmatory statistics: estimates and comparisons

Simplicity and robustness are the main principles when processing the GMP records. Non-parametric tests and summary statistics without or with negligible assumptions for the distribution patterns are highly recommended:

- Median estimates supplied with a 5th-95th percentile range and geometric mean estimated on the basis of log-transformed data with a corresponding 95% confidence interval are recommended for the summary statistics. Mann-Kendall U test, Kruskal – Wallis test, and Wilcoxon paired rank sum test are recommended for comparative analyses.
- Spearman's rank correlation coefficient is recommended for a correlation analysis.

3. Proposed outcomes of the statistical processing of GMP data

The following outcomes are proposed for the statistical processing of GMP data:

- 1) Summary statistics of atmospheric concentrations of POPs
- 2) Uncertainty analysis
- 3) Power analysis: quantification of the minimum detectable difference as a base for relevant estimates of changes over time and, if possible, time trends
- 4) Stochastic identification of time trends
- 5) Quantification of time trends

3.1 Summary statistics of atmospheric concentrations of POPs

Annually aggregated POPs concentrations, calculated as arithmetic means of the primary values can be used for both quantitative and qualitative analyses (see also section 2.2). In order to evaluate the heterogeneity of the primary data, the sample size and type of data sources have to be assessed for individual compounds. Two approaches are recommended for assessing concentration summary statistics:

- a) Median estimate reported together with a 5th-95th percentile range
- b) Geometric mean estimate based on the log-transformed annual averages with a corresponding 95% confidence interval

The variability of the baseline values can be assessed at the local, regional or global scales, merging appropriate data sets. Pooling of underlying data (both primary and aggregated), however, has to be supported by an uncertainty analysis (see 3.2).

Non-parametric tests like Mann-Kendall U test or Kruskal-Wallis test are recommended for inter-regional comparison of POPs concentrations. Parametric test like ANOVA models or analysis of covariance can be applied only after effective normalizing transformation of the concentration estimates.

3.2 Uncertainty analysis

As data reported to the GMP are typically generated by a variety of programmes, at several background sites of each UN region, they have to be inspected for an intra-regional and inter-regional homogeneity in the annually averaged POPs concentrations. Graphically, regional variability can be reported as the intra-regional 5th-95th percentile range. Sample distribution functions of the regional samples can then be compared and tested by proper robust methods (Kolmogorov-Smirnov test, Kruskal-Wallis test). The same applies for the geometric means of the averaged concentrations and their 95% confidence intervals.

The uncertainty analysis identifies regions or data subsets with increased intra-regional variability in the annually averaged concentrations and the sources of such variability (evident outlying values should be excluded). Any spatial or temporal comparison should be preceded by an assessment of internal homogeneity of concentration values in the areas of interest.

Similarly, the homogeneity should also be assessed in the time trend analysis (*i.e.* presence of and same direction in the trend change and annual difference). A year-to-year difference can be compared among time-series based on the individual sites. Such variability can be expressed as a standardized year-to-year difference or as a coefficient of variation (expressed in %). Applying time-related regression models and their residuals is possible as well. In accessible time series, homogeneity (or non-homogeneity) in a year-to-year variance indicates the degree of representativeness and stability of the identified time trends. The time series reported from various sites can be merged for more powerful trend analysis only if their homogeneity was proved.

3.3 Power analysis: quantification of minimum detectable difference

The heterogeneity and limited accessibility of primary data in the first GMP reports significantly limit the power analysis of time trends for many compounds. Time-related analysis performed on the annually aggregated data (see 2.2) partially reduces their sensitivity and the ability to detect significant differences. Therefore, any time trend analysis must be accompanied by power analysis, and the identified trends must always be reported together with the corresponding minimum detectable difference. Power analysis estimates a minimum difference between two annually aggregated concentration values detectable by paired t-test on log-transformed data ($\alpha = 0.05$ and $\beta = 0.20$). Appropriate non-parametric alternatives such as the Wilcoxon-rank-sum test or Mann-Kendall test can be used as well, especially when the analysis is based on primary concentration data rather than normalized data. This approach should be first tested in a pilot study performed on available primary data sets.

3.4 Stochastic identification of time trends

Time trends are identified via a qualitative test of statistical significance of the time-related changes observed in the consecutive measurements. At least five consecutive annually aggregated concentration values are required when assessing time trends using one of the following robust techniques:

- The Daniel's test, as an application of the Spearman's rank correlation coefficient between the concentration values and corresponding time ranks;
- The Mann-Kendal test, as a non-parametric test for detecting a trend in time series, based on binary coding of the changes in measurements consecutive in time.

The direction of the time trend (whether concentration values are increasing or decreasing in time) has to be recorded whenever it is confirmed as statistically significant. In addition, any concentration change over time should be reported in the same way, although there is no exact statistical significance

behind it. Both statistically significant and non significant time changes over time must be correctly quantified in the reports and marked with the p value generated by appropriate tests (see 3.5).

3.5 Quantification of time trends

Quantification of time trends should be performed whenever the proper statistical tests confirm significant and consistent time-related differences in POPs concentrations (see 3.4). A quantified trend means a difference $\Delta=y_1-y_2$, where y_1 and y_2 correspond to annually aggregated concentration values recorded in two consecutive years. The time-related difference in the concentration value should be expressed with the following attributes:

- The difference as an absolute value expressed in concentration units;
- The relative change (%) expressed as an index of the value detected in the baseline year;
- The 95% confidence interval of the time-related difference;
- The p value of the trend test;
- The corresponding minimum detectable annual difference.

In addition to the evaluation of the temporal changes in POPs concentrations in core matrices, it can also be useful to monitor temporal changes of their relative contribution. Such information can provide new insights into the changing primary and secondary sources or the transport pathways of POPs.

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Case Study: Evaluation of Atmospheric Concentrations of Selected POPs from the first GMP Reports

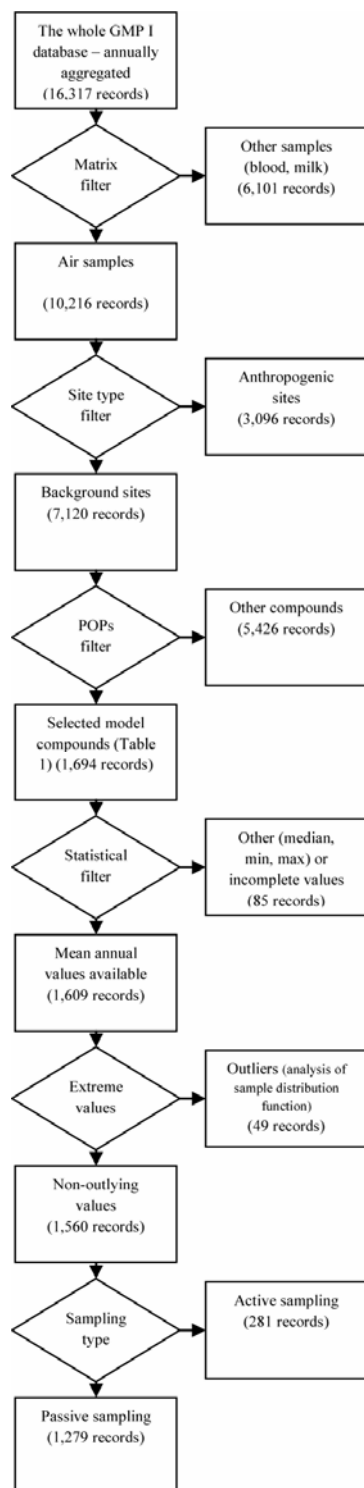


Figure 1: Six-step validation of GMP1 records

Introduction: Six Levels of Data Selection

This case study shows the outcomes of the methodology proposed in the technical note to Chapter 3 of the guidance document on a selection of data from the first GMP reports.

For a reliable assessment of the baseline POPs concentrations, a six-step validation procedure was applied on the annually aggregated GMP1 data. This procedure was introduced in order to maintain a high predictive value of the GMP1 records and to avoid bias in the concentration values.

The initial data filtering stratified the records by objective entities such as the sampling matrix, site type and compounds analyzed, and subsequently excluded apparently extreme or unreliable values from the quantitative analysis.

This case study is focused on POPs concentrations in ambient air. Other matrices reported in GMP1 - breast milk and blood - were not included. Therefore, in the first step, only 10,216 records reported from atmospheric monitoring were selected from a total of 16,317 records.

The second validation step verified the relevance and completeness in the identification of the sampling site (spatially aggregated atmospheric samples were excluded, except for the GRULAG region, where they were aggregated over the remote background sites). The subsequent analysis considers only clearly coded background sites: sampling sites with increased pollution stemming from industry, transport or agricultural production were filtered out. These controls resulted in a smaller sub-set of 7,120 records reported from well-described background sites.

In the third step, the procedure separated 1,694 records of selected substances that were well-represented in GMP1 to estimate their concentrations. Among the initial 12 legacy POPs reported in GMP1, DDTs (*p,p'*-DDT and *p,p'*-DDE), hexachlorobenzene (HCB) and a sum of 6 polychlorinated biphenyls (PCBs) were selected. In addition, among the newly listed POPs, alpha-HCH and gamma-HCH were also reported frequently. Subsequently, a further selection was carried out according to the accessibility of time series data for pilot estimates of historical time trends and changes over time. At least one time series with five consecutive measurement years at minimum one site was required for this purpose.

The fourth step – statistical filter - removed 85 records, where the atmospheric concentration was expressed by another statistical characteristic than the mean value of the measurements realized during the one-year period (*i.e.* percentiles, minimum, maximum, median estimates and values that covered unclear periods of time were excluded).

The fifth step excluded statistically verified extreme values, *i.e.* points exceeding the 95th percentile in computer-assisted reconstruction of log-normal distribution of primary values.

The final pool of data consisted of 1,560 records that were classified according to the sampling method, *i.e.* active and passive samples. Statistical analysis was separately performed for these two groups.

Table 1: Parameters selected for the pilot GMP1 analysis*

<i>p,p'</i> -DDT	sum of 6 polychlorinated biphenyls (PCB): PCB 28 (2,4,4'-trichlorobiphenyl) PCB 52 (2,2',5,5'-tetrachlorobiphenyl) PCB 101 (2,2',4,5,5'-pentachlorobiphenyl) PCB 138 (2,2',3,4,4',5'-hexachlorobiphenyl) PCB 153 (2,2',4,4',5,5'-hexachlorobiphenyl)
<i>p,p'</i> -DDE	
hexachlorobenzene (HCB)	
α -hexachlorocyclohexane	
γ -hexachlorocyclohexane	

* These compounds were included in the model training data set to demonstrate the validity of the proposed methodology. The selection of POPs for the analysis was based on the list of 12 initial POPs reported in GMP1 with respect to the availability of data. Furthermore, among the newly listed POPs, α -HCH and γ -HCH were also included, since the volume of GMP1 data for these compounds was large enough to enable reliable analysis.

Statistical methodology

The statistical analysis was carried out for 5 individual parameters listed in Table 1 and separately for the sum of the six indicator PCB congeners. Quantitative and qualitative analyses were solely performed on the annually aggregated concentration values reported in GMP1 or obtained from GMP1 primary data by arithmetic mean. All statistical calculations were applied on the basis of standard and robust methods, without excessive requirements on the sample size or the shape of sample distribution of primary values.

The sample size and range of data sources were assessed for each parameter. This step is very important for clarifying the heterogeneity of the primary GMP1 records, as some compounds were reported from several regions/sites, while others were adequately reported only from one site. The following descriptive items were evaluated and summarized:

- Data source: information on the site/laboratory/project reporting the data. In the case of a single source, this is directly identified. If data are combined from several reporting units for a more robust estimation, the “multiple reports” code is used.
- Period: time span (in years) for which data assessment can take place.
- No. of records: sample size used for the calculation of the relevant statistical quantity.
- Value: the value of the statistical quantity (*e.g.* quantified concentrations, time trend, etc.), if available; otherwise the "N/A" code was used.

The following five statistical measures were examined as key endpoints:

1. **Summary statistics of POPs concentrations.** A robust set of descriptive statistics based on selected data records was applied in the computation of:
 - a. Regional median supplemented by 5th and 95th percentile: computed for all records over the accessible sampling period. This value describes the overall range of all values and serves as a robust description of the central tendency in the sample data distribution.
 - b. Regional geometric mean and its 95% confidence interval: computed over the accessible sampling period. It provides a parametric estimate of the concentration based on the assumption of lognormal distribution of values.
 - c. Regional arithmetic mean: provides a supplementary description of the concentration values in the region over the accessible sampling period. This procedure was used as a quantitative estimate, although the sample distributions do not correspond to the normal distribution model.
2. **Detectable alternative for time trend estimates**, expressed as the minimum detectable annual difference, was estimated in available time series using power analysis for the minimum statistically significant detectable difference of two arithmetic means (annually averaged concentration values) in paired t-test with $\alpha = 0.05$ and power = 0.80.

The dataset for the computation of the variability of annual differences was prepared using the following procedure:

The difference between the start and the end of the series was computed, and t divided by the length of the time series, to obtain average annual differences for each site with at least two concentration values available. The standard deviation of the differences were used as input to

standard power analysis of the paired t-test together with a desired power = 0.80 (1 – β) and α = 0.05; the paired t-test was selected as a standard test for analysing the differences in the situation, where the computed differences follow a normal distribution; this was also valid when primary concentration data were log-normally distributed.

The computation is based on the following formula:

$$DA = \frac{t_{1-\alpha/2}^v \times SD}{\sqrt{N}}$$

where DA is estimated detectable alternative, SD represents the standard deviation of the differences, t^v is value of Student's distribution for given power, α represents the degrees of freedom ($n=v-1$).

3. **Time trend identification**, as a qualitative test which confirms a consistent time trend among the consecutive POPs values in terms of statistical significance. Robust Mann-Kendall tests were used. The evaluation was applicable only to sites with at least five consecutive annually aggregated mean concentration values available. α = 0.05 was used as a level of statistical significance in all tests.

The Mann-Kendall test (Mann, 1945; Kendall, 1975) is a non-parametric test for identifying trends in time series data. The test compares the relative magnitudes of sample data instead of the exact values. The main benefit of this test is that data do not need to conform to any particular distribution. Moreover, data reported as not-detected can be included in the test by replacing them with a common value smaller than the smallest measured value in the data set. The procedure assumes that there is only one data value per each point in time. The median is used for multiple data points over a single time period.

The data values are evaluated as ordered time series. Each data value is compared to all subsequent data values. The initial value of the Mann-Kendall statistics, S , is assumed to be 0 (*e.g.*, no trend). If data value from a subsequent time period is higher, S is incremented by 1. On the other hand, if the data value from a later time period is lower than a data value sampled earlier, S is diminished by 1. The net result of all such increments and decreases yields the final value of S .

Let x_1, x_2, \dots, x_n represent n data points where x_j represents the data point at time j .

Then the Mann-Kendall statistics (S) is given by

$$S = \sum_{k=1}^{n-1} \sum_{j=k+1}^n \text{sign}(x_j - x_k),$$

where

$$\text{sign}(x_j - x_k) = \begin{cases} 1 & \text{if } x_j - x_k > 0 \\ 0 & \text{if } x_j - x_k = 0. \\ -1 & \text{if } x_j - x_k < 0 \end{cases}$$

A high positive value of S is an indicator of an increasing trend, and a low negative value indicates a decreasing trend. However, it is necessary to compute the probability associated with S and with the sample size, n , to statistically quantify the significance of the trend.

The variance of S is defined as

$$\text{VAR}(S) = \frac{1}{18} \left[n(n-1)(2n+5) - \sum_{p=1}^g t_p(t_p-1)(2t_p+5) \right],$$

where n is the number of data points, g is the number of tied groups (a tied group is a set of sample data having the same value), and t_p is the number of data points in the p^{th} group. For example, in the model sequence {2, 3, non-detect, 3, non-detect, 3}, $n=6$, $g=2$, $t_1=2$ for the non-detects, and $t_2=3$ for the tied value 3.

Now a normalized test statistic Z can be computed as follows:

$$Z = \begin{cases} \frac{S-1}{\sqrt{VAR(S)}} & \text{if } S > 0 \\ 0 & \text{if } S = 0 \\ \frac{S+1}{\sqrt{VAR(S)}} & \text{if } S < 0 \end{cases}$$

The trend is considered as decreasing if Z is negative and the computed probability is higher than the level of significance. The trend is considered as increasing if Z is positive and the computed probability is higher than the level of significance. If the computed probability is lower than the level of significance, there is no trend.

4. **Time trend quantification** is computed using linear regression slope estimate. The quantified trend represents the mean annual change based on a linear model and supplemented by its 95% confidence interval. Simple linear regression (Zar, 1998) for time series trend estimate is defined as:

$$Y_i = \alpha + \beta X_i + \varepsilon_i,$$

where α and β are constants and ε_i is referred to as an “error” or “residual”. The parameter β is also called the regression coefficient, or the slope, or the trend estimate in time series analysis and the parameter α is called the Y intercept. If the estimate for β is b and the best estimate for α is a , then the sample regression equation is written as:

$$\hat{Y}_i = a + bX_i.$$

The trend, b , of the regression line computed from sample data expresses quantitatively the straight-line dependence of Y and X in the sample. It is possible to obtain a sample of data points (*i.e.* by random sampling) where the calculated b would suggest that β was positive, even though it is, in fact, zero. It is unlikely to obtain points to yield $\beta=0$ by random sampling. To demonstrate the likelihood, we can examine the null hypothesis, $H_0 : \beta = 0$, and the alternate hypothesis, $H_A : \beta \neq 0$. Thus, if the probability of obtaining the calculated b is small (let's say 5% or less), then H_0 is rejected, and H_A is assumed to be true. This null hypothesis concerning β can be tested for example by using Student's t statistic.

The $(1-\alpha)$ confidence interval can be calculated for the parameter being estimated (β) using Student's t statistic as:

$$b \pm t_{\alpha(2), (n-2)} s_b,$$

where s_b is the standard error of b and is calculated using the residual mean square, which is often written as $s_{Y.X}^2$,

$$s_b = \sqrt{\frac{s_{Y.X}^2}{\sum x^2}}.$$

The residual mean square depends on the residual sum of squares and the residual degree of freedom as follows

$$residualSS = \sum (Y_i - \hat{Y}_i)^2$$

$$residualDF = totalDF - regressionDF$$

$$s_{Y.X}^2 = residualSS / residualDF,$$

When working with simple linear regression, $regressionDF$ equals 1 and $totalDF$ is $n-1$, thus $residualDF$ equals $n-2$, where n denotes number of observations.

Results – air monitoring using passive sampling

Table 2 contains aggregated entries summarizing data sources for the statistical analysis performed, *i.e.* the sites where relevant passive sampling data were available. After undergoing the six-step validation, the entire data set consists of 1,279 entries from all UN regions. The cell is shaded if there are no data entries available.

Table 2: Accessible data sources for air monitoring using passive sampling

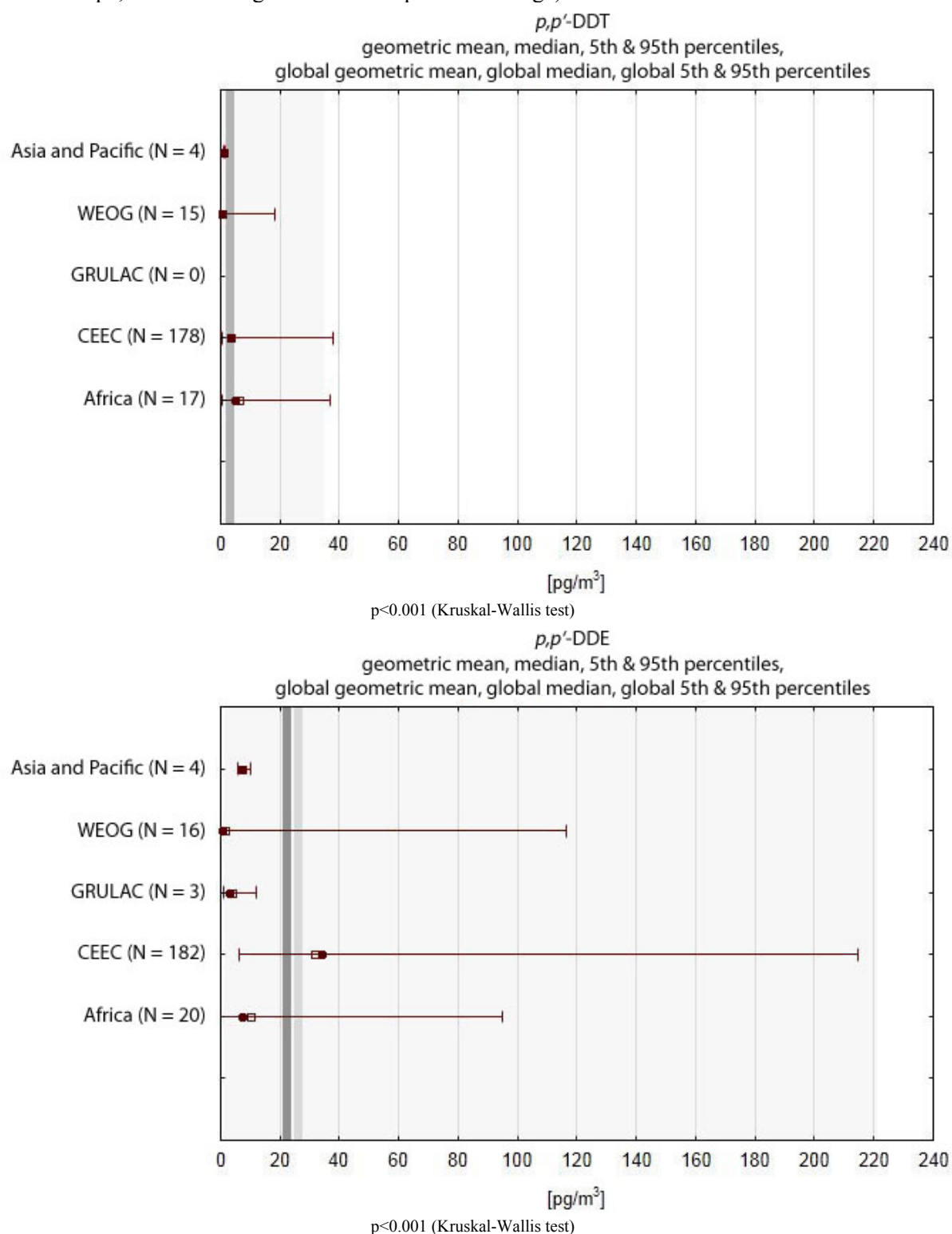
Compound	Africa	CEEC	GRULAC	WEOG	Asia and Pacific
<i>p,p'</i>-DDT	Total countries: 10 Total sites: 20 Total records: 17 2005–2008	Total countries: 21 Total sites: 148 Total records: 178 2003–2008	Total countries: 0 Total sites: 0 Total records: 0	Total countries: 9 Total sites: 15 Total records: 15 2005	Total countries: 1 Total sites: 2 Total records: 4 2006–2007
<i>p,p'</i>-DDE	Total countries: 11 Total sites: 21 Total records: 20 2005–2008	Total countries: 21 Total sites: 148 Total records: 182 2003–2008	Total countries: 2 Total sites: 2 Total records: 3 2005–2008	Total countries: 9 Total sites: 16 Total records: 16 2005	Total countries: 1 Total sites: 2 Total records: 4 2006–2007
HCB	Total countries: 10 Total sites: 17 Total records: 17 2008	Total countries: 21 Total sites: 146 Total records: 180 2003–2008	Total countries: 0 Total sites: 0 Total records: 0	Total countries: 0 Total sites: 0 Total records: 0	Total countries: 1 Total sites: 2 Total records: 4 2006–2007
Σ 6 PCB	Total countries: 10 Total sites: 17 Total records: 17 2006–2008	Total countries: 21 Total sites: 146 Total records: 174 2003–2008	Total countries: 0 Total sites: 0 Total records: 0	Total countries: 0 Total sites: 0 Total records: 0	Total countries: 1 Total sites: 2 Total records: 4 2006–2008
α-HCH	Total countries: 10 Total sites: 17 Total records: 12 2008	Total countries: 21 Total sites: 48 Total records: 180 2003–2008	Total countries: 0 Total sites: 0 Total records: 0	Total countries: 10 Total sites: 19 Total records: 28 2005–2006	Total countries: 1 Total sites: 2 Total records: 4 2006–2007
γ-HCH	Total countries: 10 Total sites: 17 Total records: 13 2008	Total countries: 21 Total sites: 48 Total records: 175 2003–2008	Total countries: 0 Total sites: 0 Total records: 0	Total countries: 10 Total sites: 19 Total records: 28 2005–2006	Total countries: 1 Total sites: 2 Total records: 4 2006–2007

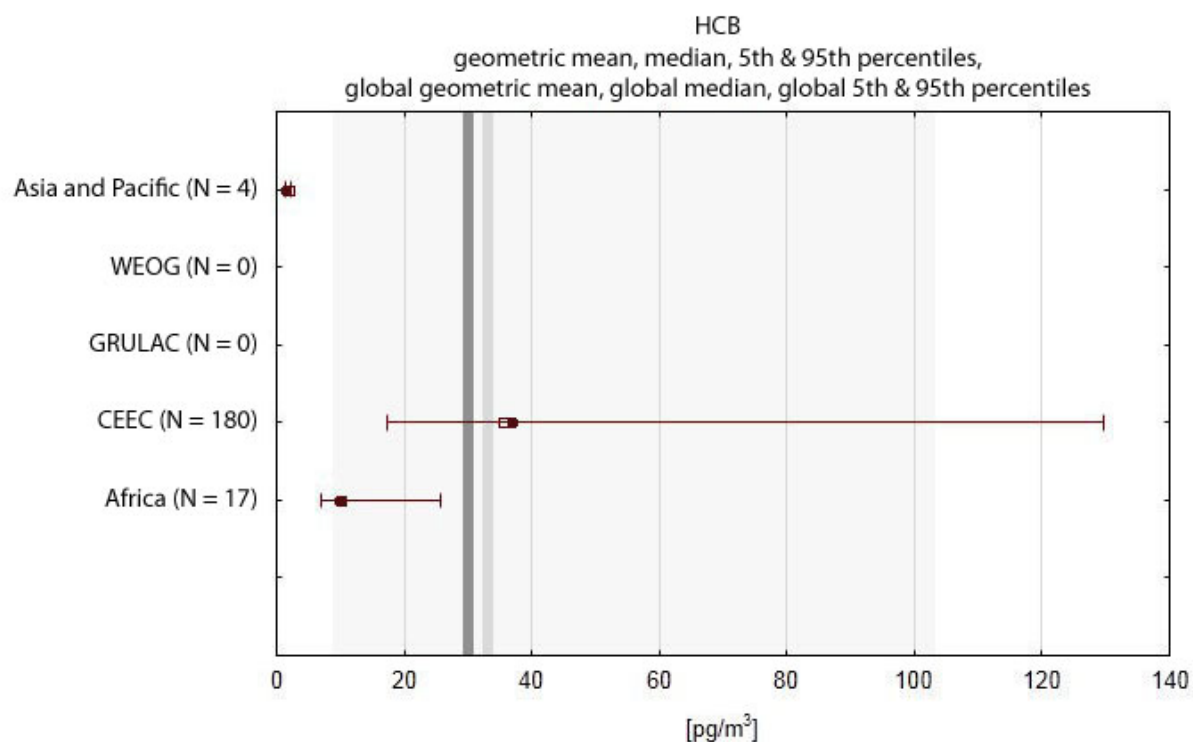
Records: Annual POPs concentration values aggregated from primary records by arithmetic mean.

The statistical summary is complemented by the variability/uncertainty analysis as shown in Figure 2, consisting of six parts, each focusing on the individual parameter (compound) in the analysis.

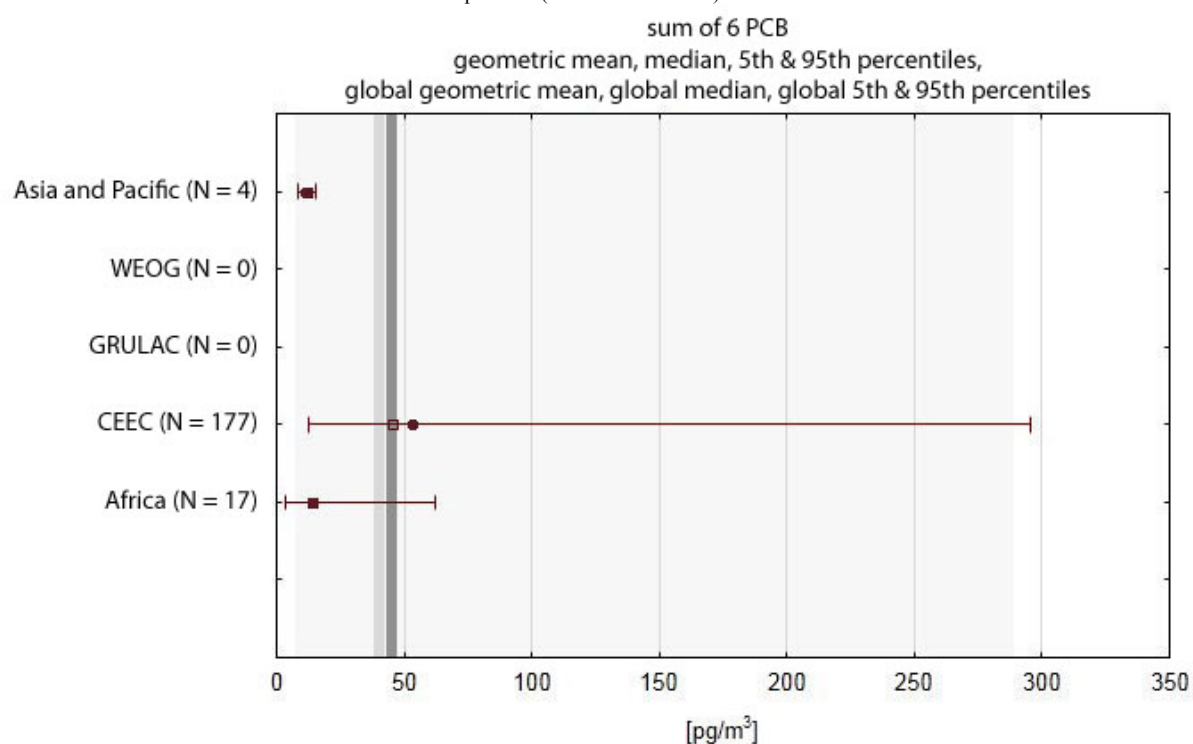
The analysis compares median and geometric mean estimates and their variability among the individual UN regions. The boxes in the charts indicate medians and the circles geometric means of the data sets from the individual regions; whiskers correspond to the 5th–95th percentile range. The shaded area chart corresponds to the 5th – 95th percentile range of the entire set of sites for all regions; the grey vertical stripe corresponds to the global median estimate and the black vertical stripe corresponds to the global geometric mean estimate of this set.

Figure 2: Variability analysis of the atmospheric concentrations of POPs in the five UN regions, air monitoring by passive samplers (regional median: boxes; regional geometric mean: circles; regional 5th – 95th percentile ranges: whiskers; global median: grey vertical stripe; global geometric mean: black vertical stripe; shaded area: global 5th – 95th percentile range).





p<0.001 (Kruskal-Wallis test)



p<0.001 (Kruskal-Wallis test)

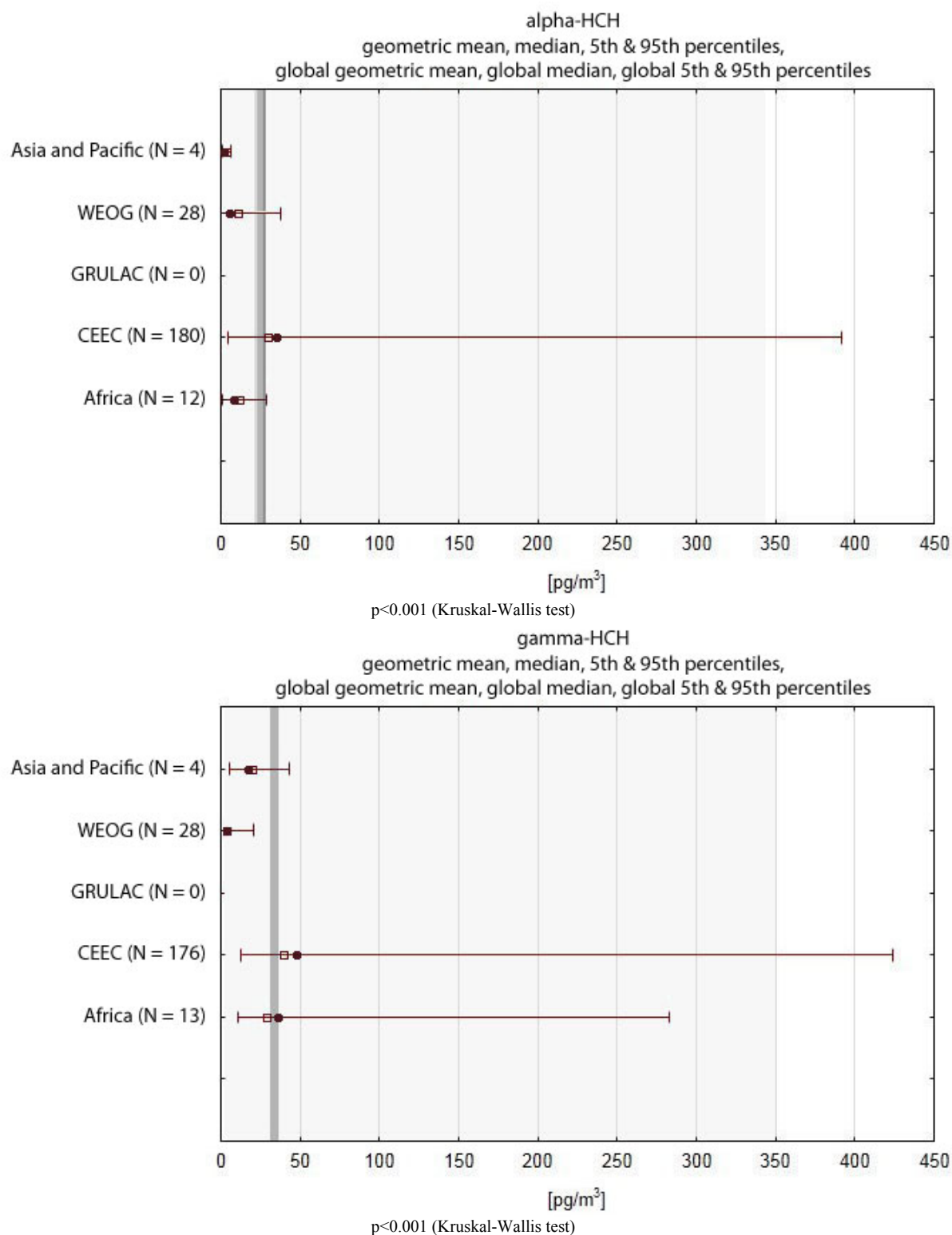


Table 3 displays the results of the statistical analysis of validated atmospheric POPs concentrations obtained by passive sampling.

Table 3: Data summary for air monitoring using passive samplers

Compound	POPs concentrations: summary statistics	Detectable alternative	Historical time trends	
			trend indication	trend quantification
<i>p,p'</i> -DDT	Source: All; Period: 2003–2008; Records: 214 Median (5-95 th percentile): 3.14 (0.350–34.8) pg/m ³ Geometric mean (95% CI): 3.29 (2.78–3.89) pg/m ³ Mean (standard deviation): 7.21 (11.5) pg/m ³	Source: All Period: 2003–2008 Sites: 23 Value: 2.06 pg/m ³ /y	Source: Košetice Period: 2003–2008 Records total: 6 Value: N	Source: Košetice Period: 2003–2008 Records total: 6 Value (95% CI): -0.5 (-1.7; 0.8) pg/m ³ /y
<i>p,p'</i> -DDE	Source: All; Period: 2003–2008; Records: 225 Median (5-95 th percentile): 25.6 (1.20–201) pg/m ³ Geometric mean (95% CI): 22.1 (17.9–27.3) pg/m ³ Mean (standard deviation): 52.6 (72.0) pg/m ³	Source: All Period: 2003–2008 Sites: 24 Value: 10.6 pg/m ³ /y	Source: Košetice Period: 2003–2008 Records total: 6 Value: N	Source: Košetice Period: 2003–2008 Records total: 6 Value (95% CI): -0.9 (-3.8; 2.0) pg/m ³ /y
HCB	Source: All; Period: 2003–2008; Records: 201 Median (5-95 th percentile): 32.8 (8.69–103) pg/m ³ Geometric mean (95% CI): 31.2 (28.1–34.7) pg/m ³ Mean (standard deviation): 41.5 (42.4) pg/m ³	Source: All Period: 2003–2008 Sites: 23 Value: 13.1 pg/m ³ /y	Source: Košetice Period: 2003–2008 Records total: 6 Value: Y	Source: Košetice Period: 2003–2008 Records total: 6 Value (95% CI): -37.0 (-57.7; -16.3) pg/m ³ /y
Σ 6 PCB	Source: All; Period: 2003–2008; Records: 189 Median (5-95 th percentile): 39.5 (8.79–289) pg/m ³ Geometric mean (95% CI): 44.6 (38.4–51.8) pg/m ³ Mean (standard deviation): 79.5 (100) pg/m ³	Source: All Period: 2003–2008 Sites: 19 Value: 32.9 pg/m ³ /y	Source: Košetice Period: 2003–2008 Records total: 6 Value: N	Source: Košetice Period: 2003–2008 Records total: 6 Value (95% CI): -5.9 (-18.8; 7.1) pg/m ³ /y
α-HCH	Source: All; Period: 2003–2008; Records: 224 Median (5-95 th percentile): 22.8 (1.35–343) pg/m ³ Geometric mean (95% CI): 24.3 (19.7–30.0) pg/m ³ Mean (standard deviation): 69.1 (119) pg/m ³	Source: All Period: 2003–2008 Sites: 34 Value: 8.87 pg/m ³ /y	Source: Košetice Period: 2003–2008 Records total: 6 Value: N	Source: Košetice Period: 2003–2008 Records total: 6 Value (95% CI): -0.1 (-2.2; 2.0) pg/m ³ /y
γ-HCH	Source: All; Period: 2003–2008; Records: 221 Median (5-95 th percentile): 33.8 (2.90–350) pg/m ³ Geometric mean (95% CI): 33.3 (27.7–39.9) pg/m ³ Mean (standard deviation): 75.0 (125) pg/m ³	Source: All Period: 2003–2008 Sites: 34 Value: 8.15 pg/m ³ /y	Source: Košetice Period: 2003–2008 Records total: 6 Value: N	Source: Košetice Period: 2003–2008 Records total: 6 Value (95% CI): -1.7 (-6.3; 2.9) pg/m ³ /y

¹ The detectable alternative is expressed as the detectable mean annual difference with power = 0.8 and $\alpha = 0.05$. The computation is based on the set of sites with available trend data, which are used for the estimation of the variability of differences.

Results – air monitoring using active sampling

Table 4 contains aggregated entries summarizing data sources for the statistical analysis performed on sites with relevant active concentration data records available. The set consisted of 281 entries from all regions after the six-step validation process described in the introductory section: WEOG (81 records), Asia and Pacific (134 records) and CEEC (66 records). No valid sets were obtained from Africa and GRULAC. The respective cells are shaded if there no available data entries exist.

Table 4: Data sources for air monitoring using active sampling

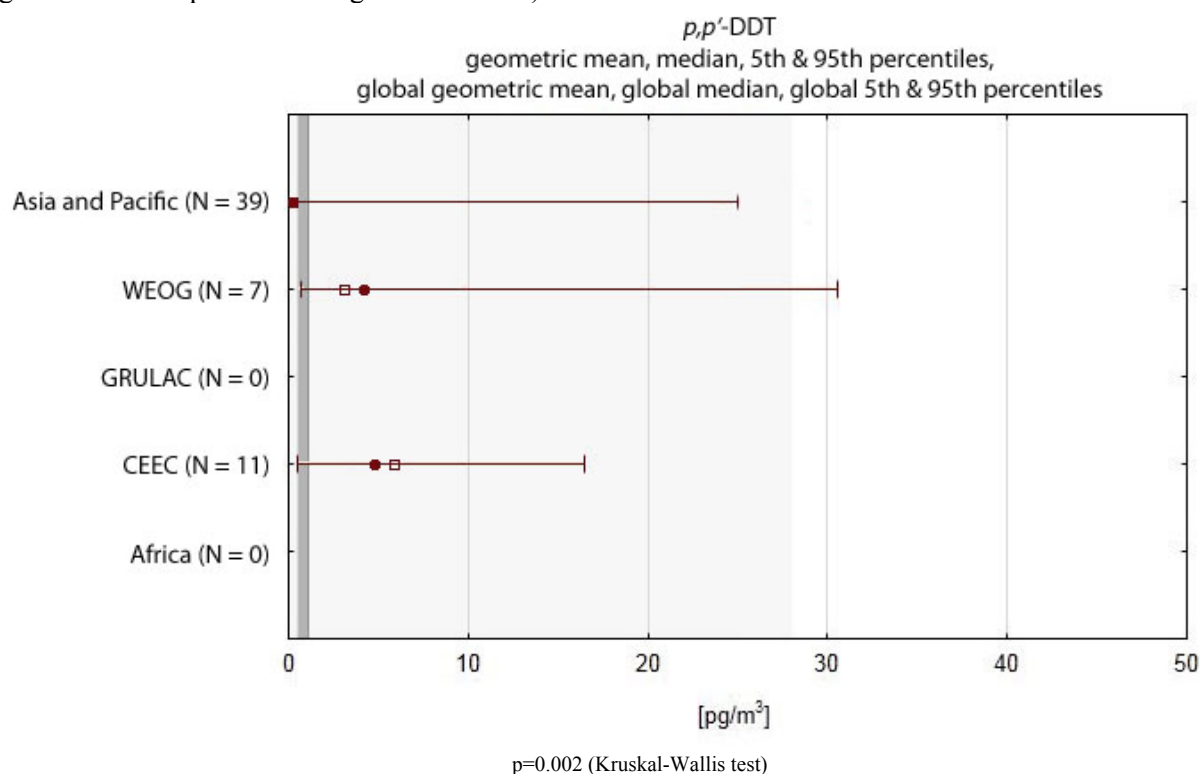
Compound	Africa	CEEC	GRULAC	WEOG	Asia and Pacific
<i>p,p'</i> -DDT	Total countries: 0 Total sites: 0 Total records: 0	Total countries: 1 Total sites: 1 Total records: 11 1998–2008	Total countries: 0 Total sites: 0 Total records: 0	Total countries: 2 Total sites: 5 Total records: 7 2003	Total countries: 9 Total sites: 33 Total records: 39 2004–2007
<i>p,p'</i> -DDE	Total countries: 0 Total sites: 0 Total records: 0	Total countries: 1 Total sites: 1 Total records: 11 1998–2008	Total countries: 0 Total sites: 0 Total records: 0	Total countries: 2 Total sites: 7 Total records: 7 2003	Total countries: 9 Total sites: 33 Total records: 39 2004–2007
HCB	Total countries: 0 Total sites: 0 Total records: 0	Total countries: 1 Total sites: 14 Total records: 11 1998–2008	Total countries: 0 Total sites: 0 Total records: 0	Total countries: 8 Total sites: 21 Total records: 48 1998–2006	Total countries: 9 Total sites: 35 Total records: 35 2004–2007

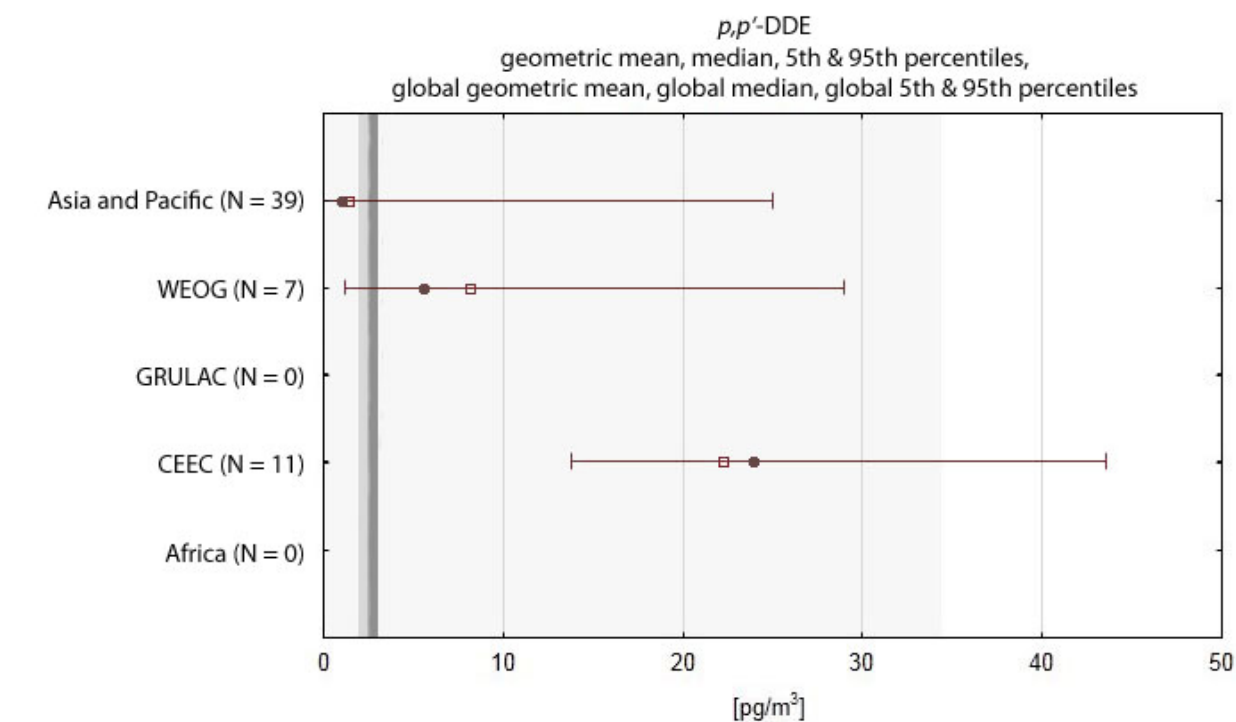
Σ 6 PCB	Total countries: 0 Total sites: 0 Total records: 0	Total countries: 1 Total sites: 1 Total records: 11 1998–2008	Total countries: 0 Total sites: 0 Total records: 0	Total countries: 3 Total sites: 3 Total records: 3 2006	Total countries: 1 Total sites: 21 Total records: 21 2004
α-HCH	Total countries: 0 Total sites: 0 Total records: 0	Total countries: 1 Total sites: 1 Total records: 11 1998–2008	Total countries: 0 Total sites: 0 Total records: 0	Total countries: 3 Total sites: 8 Total records: 8 2000–2003	Total countries: 0 Total sites: 0 Total records: 0
γ-HCH	Total countries: 0 Total sites: 0 Total records: 0	Total countries: 1 Total sites: 1 Total records: 11 1998–2008	Total countries: 0 Total sites: 0 Total records: 0	Total countries: 3 Total sites: 8 Total records: 8 2000–2003	Total countries: 0 Total sites: 0 Total records: 0

Records: annual POPs concentration values aggregated from primary records by arithmetic mean.

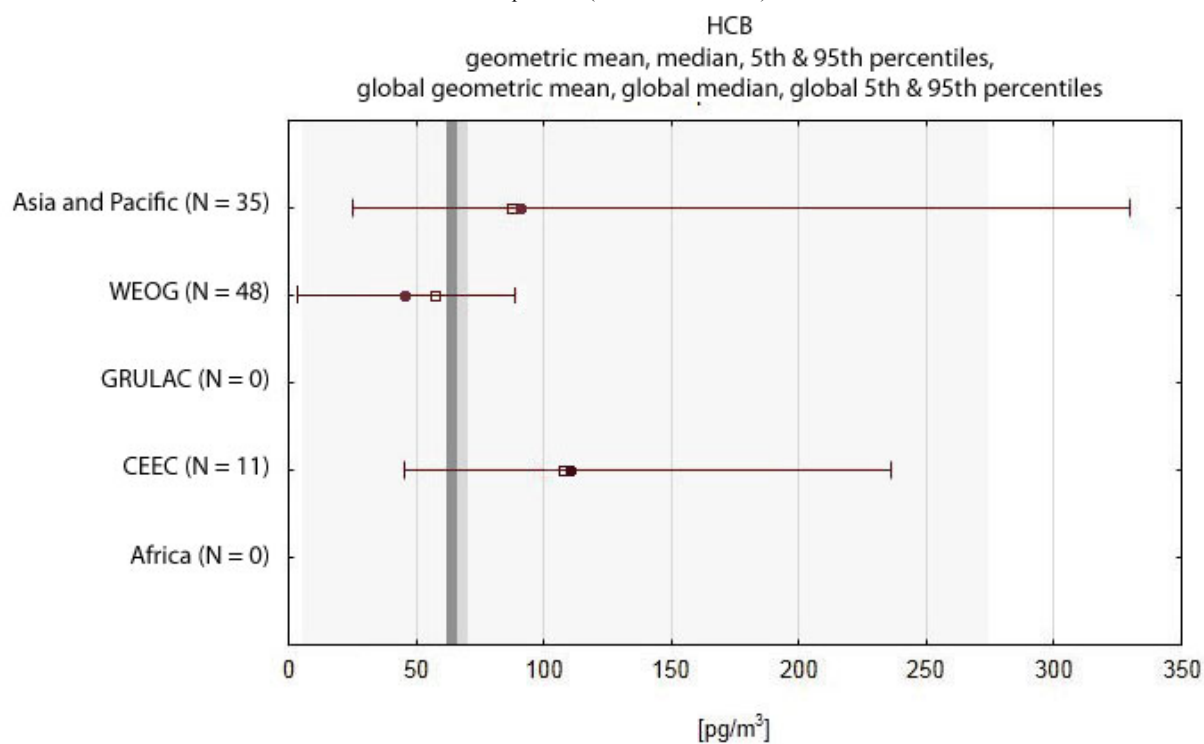
The statistical summary is complemented by the variability/uncertainty analysis provided in Figure 3, consisting of six parts, each part focusing on the individual parameters (compounds) in the analysis. The analysis compares median and geometric mean estimates and their variability among the UN regions. The boxes in the charts indicate medians and the circles geometric means of sets of values for individual regions; whiskers correspond to the 5th – 95th percentile range. The shaded area in the chart corresponds to the 5th – 95th percentile range of the entire set of sites for all regions. The grey vertical stripe corresponds to the global median estimate and black vertical stripe corresponds to the global geometric mean of this set.

Figure 3: Variability analysis of atmospheric concentrations of POPs in the five UN regions, air monitoring using active sampling (regional median: boxes; regional geometric mean: circles; regional 5th – 95th percentile ranges: whiskers; global median: grey vertical stripe; global geometric mean: black vertical stripe; global 5th – 95th percentile range: shaded area).

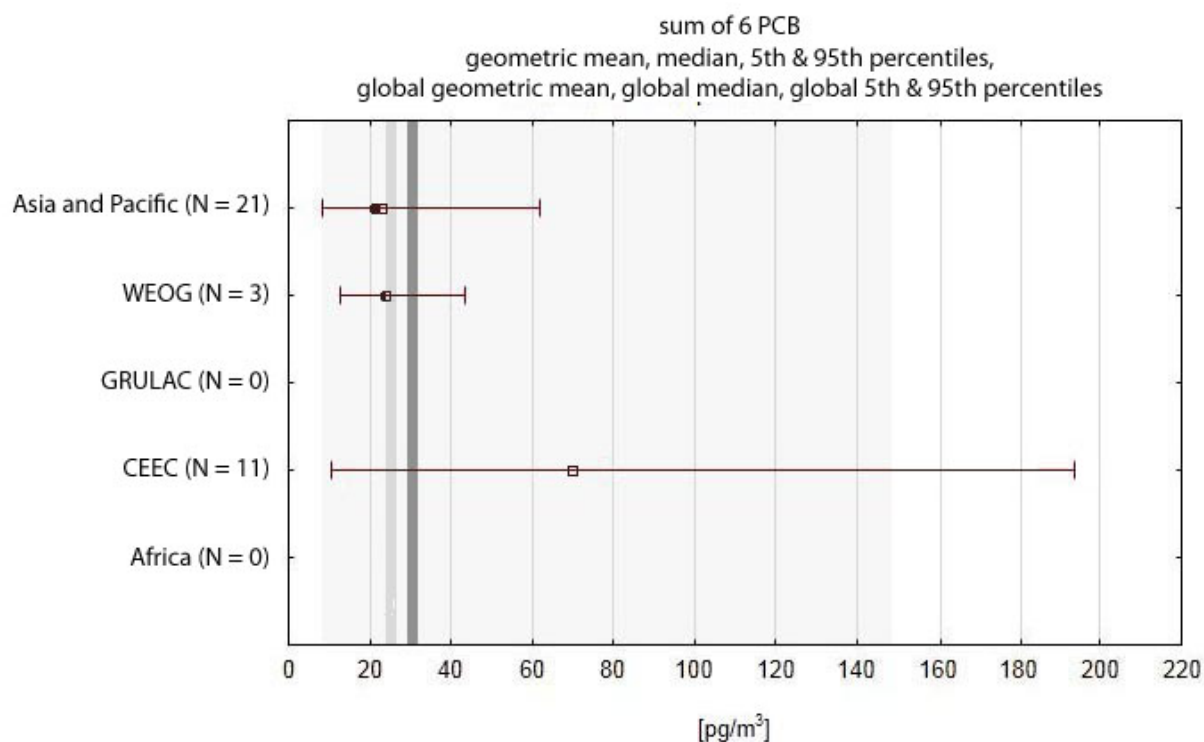




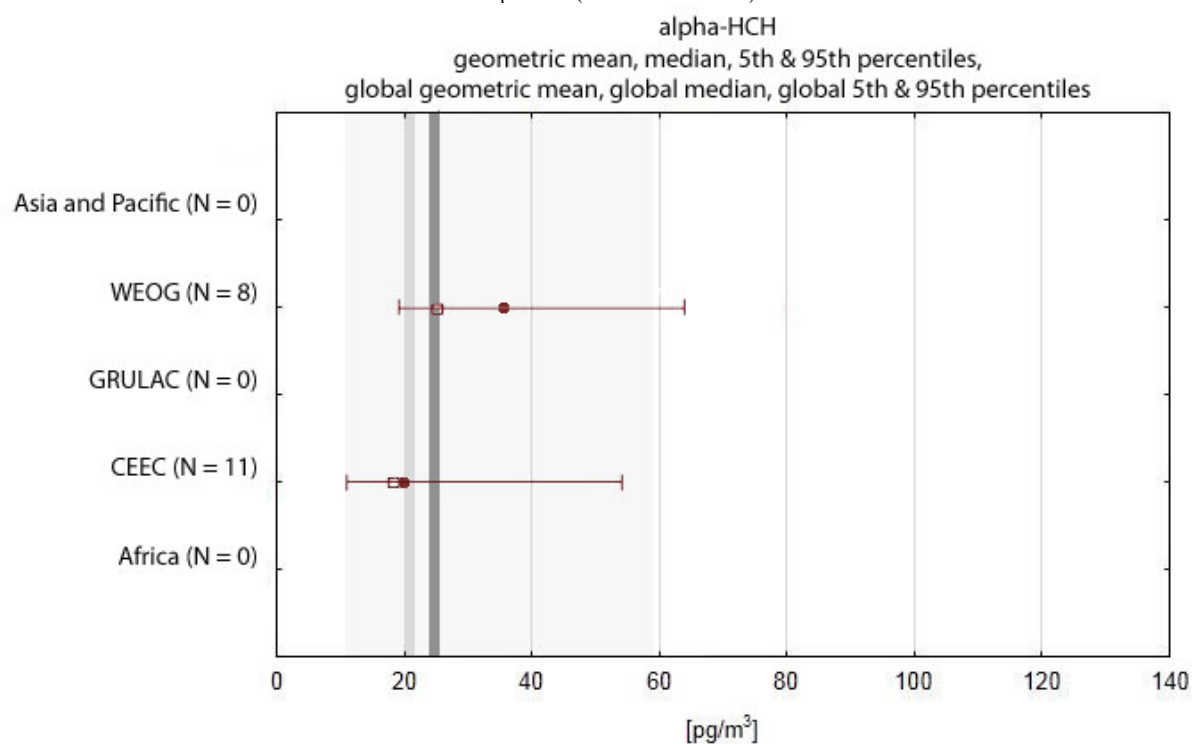
p<0.001 (Kruskal-Wallis test)



p<0.001 (Kruskal-Wallis test)



p=0.009 (Kruskal-Wallis test)



(Kruskal-Wallis test)

p=0.008

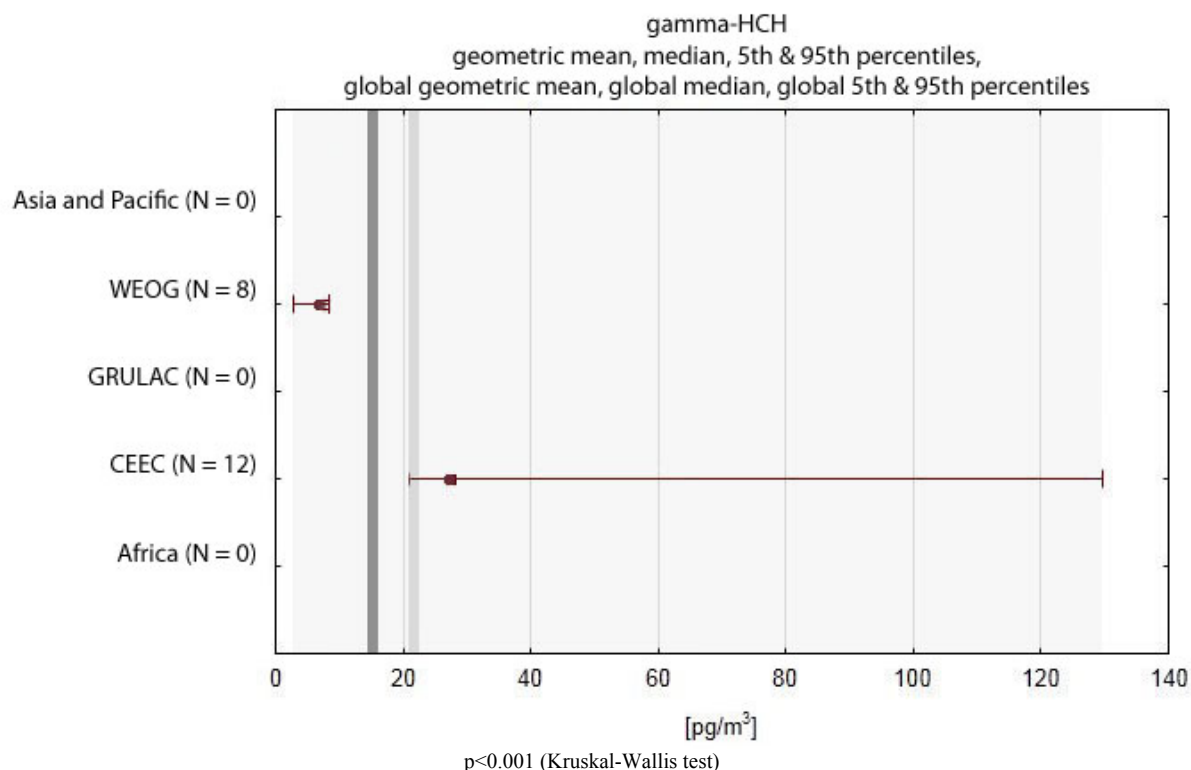


Table 5 displays the results of the statistical analysis of the validated atmospheric POPs concentrations obtained by active sampling. Both baseline concentrations and historical time trends are estimated.

Table 5: Data summary for air monitoring using active sampling

Compound	POPs concentrations: summary statistics	Detectable alternative ¹	Historical time trends	
			trend indication	trend quantification
<i>p,p'</i> -DDT	Source: All; Period: 1998–2008; Records: 45 Median (5–95 th percentile): 1.70 (3.28–8.89) pg/m ³ Geometric mean (95% CI): 1.53 (0.854–2.74) pg/m ³ Mean (standard deviation): 6.09 (9.34) pg/m ³	Source: All Period: 1998–2008 Sites: 5 Value: 5.11 pg/m ³ /y	Source: Košetice Period: 1998–2008 Records total: 11 Value: N	Source: Košetice Period: 1998–2008 Records total: 11 Value (95% CI): -0.5 (-1.7; 0.8) pg/m ³ /y
<i>p,p'</i> -DDE	Source: All; Period: 1998–2008; Records: 58 Median (5–95 th percentile): 2.11 (0.050–34.4) pg/m ³ Geometric mean (95% CI): 2.61 (1.52–4.49) pg/m ³ Mean (standard deviation): 10.1 (15.6) pg/m ³	Source: All Period: 1998–2008 Sites: 4 Value: 5.34 pg/m ³ /y	Source: Košetice Period: 1998–2008 Records total: 11 Value: Y	Source: Košetice Period: 1998–2008 Records total: 11 Value (95% CI): -0.9 (-3.8; -2.0) pg/m ³ /y
HCB	Source: All; Period: 1998–2008; Records: 93 Median (5–95 th percentile): 66.7 (5.80–236) pg/m ³ Geometric mean (95% CI): 58.7 (47.9–71.8) pg/m ³ Mean (standard deviation): 84.9 (82.2) pg/m ³	Source: All Period: 1998–2008 Sites: 11 Value: 64.8 pg/m ³ /y	Source: Košetice Period: 1998–2008 Records total: 11 Value: N	Source: Košetice Period: 1998–2008 Records total: 11 Value (95% CI): -37.0 (-57.7; -16.3) pg/m ³ /y
Σ 6 PCB	Source: All; Period: 1998–2008; Records: 35 Median (5–95 th percentile): 24.9 (8.20–149) pg/m ³ Geometric mean (95% CI): 29.9 (21.9–40.7) pg/m ³ Mean (standard deviation): 44.7 (44.6) pg/m ³	Source: Košetice Period: 1998–2008 Sites: 1 Value: N/A	Source: Košetice Period: 1998–2008 Records total: 11 Value: Y	Source: Košetice Period: 1998–2008 Records total: 11 Value (95% CI): -5.9 (-18.8; -7.1) pg/m ³ /y
α-HCH	Source: All; Period: 1998–2008; Records: 19 Median (5–95 th percentile): 21.1 (10.9–64.0) pg/m ³ Geometric mean (95% CI): 23.0 (18.2–29.1) pg/m ³ Mean (standard deviation): 26.0 (14.6) pg/m ³	Source: All Period: 1998–2008 Sites: 3 Value: 29.1 pg/m ³ /y	Source: Košetice Period: 1998–2008 Records total: 11 Value: N	Source: Košetice Period: 1998–2008 Records total: 11 Value (95% CI): -0.1 (-2.2; 2.0) pg/m ³ /y
γ-HCH	Source: All; Period: 1998–2008; Records: 19 Median (5–95 th percentile): 21.2 (11.2–40.0) pg/m ³ Geometric mean (95% CI): 15.3 (9.14–25.6) pg/m ³ Mean (standard deviation): 25.6 (29.8) pg/m ³	Source: All Period: 1998–2008 Sites: 3 Value: 13.4 pg/m ³ /y	Source: Košetice Period: 1998–2008 Records total: 11 Value: N	Source: Košetice Period: 1998–2008 Records total: 11 Value (95% CI): -1.7 (-6.3; 2.9) pg/m ³ /y

¹ The detectable alternative is expressed as the detectable mean annual difference with power = 0.8 and $\alpha = 0.05$. The computation is based on the set of sites with available trend data, which are used for the estimation of the variability of time-related differences.

Conclusions

- This pilot study was performed on a sub-set of ambient air data from the first GMP reports with the aim to demonstrate the applicability of the proposed methodology for assessing of the baseline atmospheric levels of POPs.
- Only data directly reported in GMP1 were used in this pilot study. In future assessments, these should be complemented with data available in other databases, which are only referenced in the GMP reports.
- The time trend analysis was illustrated on the data set from Kosetice in the CEE region. This site provides sufficient data from both active and passive air sampling. The minimum detectable change was determined using this data set, and temporal trends were identified and quantified.
- The selected methods identified several statistically significant decreasing time trends (*p,p'*-DDE and $\Sigma 6$ PCB in the active air samples; and HCB in the passive air samples) but also some non-significant decreasing time-related changes in POPs concentrations.

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