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.

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
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-para-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-para-dioxin
TEF	Toxic equivalency factor
TEQ	Toxicity equivalents
UNECE	United Nations Economic Commission for Europe
UNEP	United Nations Environment Programme
WHO	World Heath 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[1] capable to analyze PCDD/PCDF and dioxin-like PCB at ultra-trace concentrations: must be a 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)

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

Phase II	Activities to support the Article 16 effectiveness evaluation after 2009 (also termed as subsequent evaluations)
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

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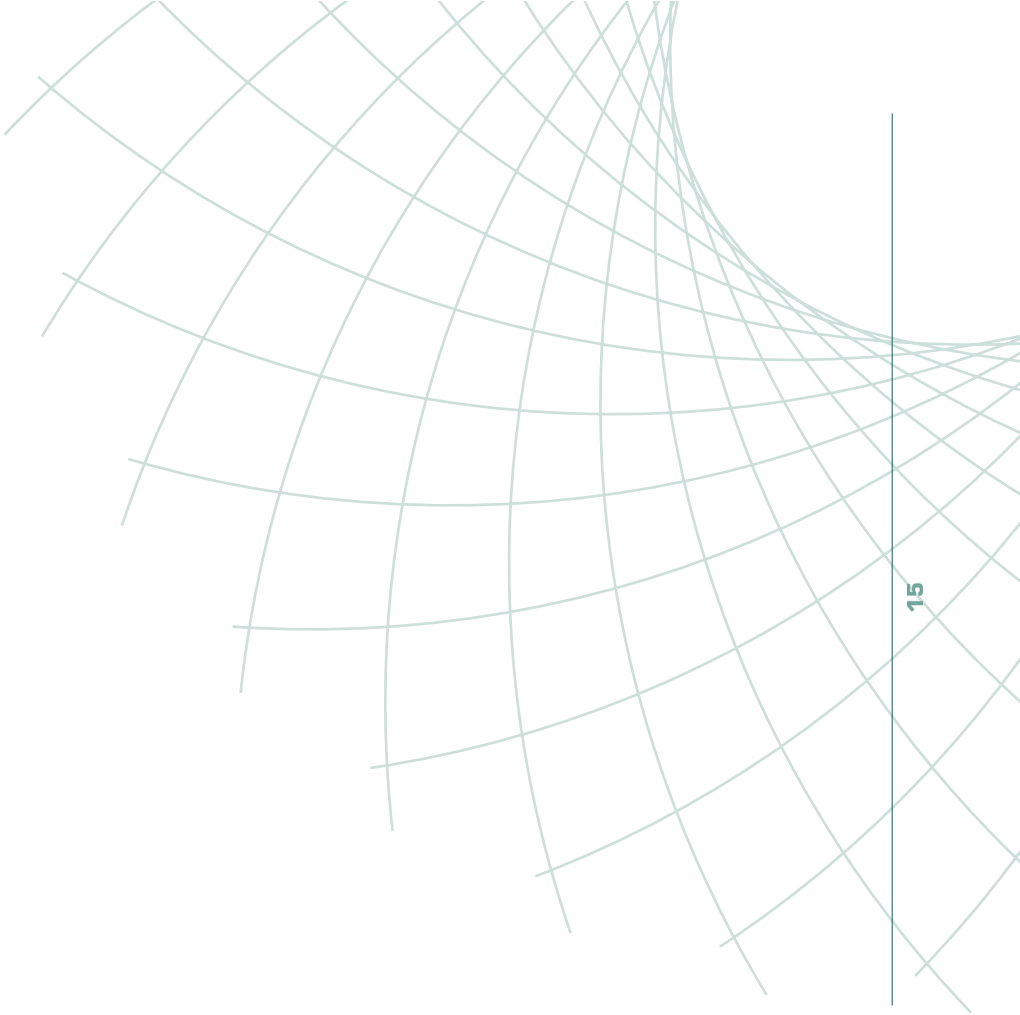
Sampling, storage, transportation, and analytical details for maternal blood (source: Centre de toxicologie du Québec / INSPQ) (electronic only).

Annex 4
Fourth WHO-Coordinated Survey of Human Milk for Persistent Organic Pollutants in Cooperation with UNEP (electronic only).

Annex 5
Standard operation procedures and protocols for air monitoring (electronic only)

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

1. Background and objectives

The Stockholm Convention on Persistent Organic Pollutants (POPs) (UNEP, 2001) entered into force 17 May, 2004. As of 28 February 2007 the Convention had 142 Parties. The major features of the Convention are summarized in "Ridding the world from POPs" (UNEP, 2002), a layman's guide to the Stockholm Convention available in the six official languages of the United Nations.

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.

To initiate consideration of this task UNEP Chemicals hosted a workshop to develop a POPs Global Monitoring Programme to support the effectiveness evaluation of the Stockholm Convention on POPs, held in Geneva in March 2003 (UNEP, 2003). The outcome of this workshop was a set of conclusions and recommendations for the elements to be contained within a global programme, upon which the first edition of the guidance document for a Global Monitoring Programme was prepared and published, in 2004, by UNEP Chemicals.

The Conference of the Parties has decided at its second meeting (Decision SC-2/13) to complete the first effectiveness evaluation at its fourth meeting in 2009, and has agreed upon the essential modalities for the environmental monitoring component of the first evaluation. The decision included agree-

ment to implement the elements of a global monitoring plan as proposed in an annex to that decision. It also established a Provisional Ad-hoc Technical Working Group (TWG) consisting of 15 representatives of Parties of the five United Nations regions to elaborate elements of the plan and its implementation to support the first effectiveness evaluation for consideration by the Conference of the Parties at its third meeting. The Conference of the Parties also decided upon the essential features of the Global Monitoring Plan (GMP) and requested the TWG to coordinate and oversee its initial regional implementation.

It further requested the Provisional Ad-hoc Technical Working Group to develop guidance on standardization (the draft guidance document on the Global Monitoring Plan), taking into account the available guidance document produced by UNEP Chemicals in 2004. Originally that document was produced for another model of a global monitoring programme which is no longer consistent with the decision of the Conference of the Parties. Revision of that document was required to ensure compatibility with the current emerging Global Monitoring Plan and draft implementation plan. The intent of the draft guidance document is to provide technical guidance on all aspects of implementation of the Global Monitoring Plan, including issues related to statistics, sampling, sample preparation, analytical methodology and data management.

Revisions to the guidance document were undertaken by a small group of experts specialized in the various document sections including experts who prepared the original document, organised and facilitated by the Stockholm Convention Secretariat. As part of the statistical considerations, the experts provided advice on what was appropriate and sufficient comparable data for the regional evaluation of effectiveness of the Convention.

1.1 The objectives of the POPs Global Monitoring Plan

To evaluate whether the POPs actually were *reduced* or *eliminated* as requested in 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 will form one of the components of information to be compiled by 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 programme 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 evaluations of effectiveness to be undertaken by the Conference of the Parties. The information to be included in the first monitoring report will be largely dependant on existing programmes and here the opportunities for the guidance document to change procedures may be limited.

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 will 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 will also be 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-2/13). It will also help 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.

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 decision SC-2/13; the Global Monitoring Plan and its implementation plan for the first evaluation; the guidance document, and media specific protocols on methodology.

This revised edition of the guidance document is focused upon the requirements of preparing for the first effectiveness evaluation in 2009. However, the first monitoring report will provide information that will in the future help to indicate whether changes in environmental levels of the listed POPs can be detected. Therefore the document also looks to the future. It is 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 Preliminary Ad-hoc Technical Working Group. The most recent versions of these documents are available at http://www.pops.int/documents/meetings/cop_3/meetingdocs/default.htm

1.3 General principles

The framework developed by the Preliminary Ad-hoc Technical Working Group for the Global Monitoring Plan closely follows the direction given by the Conference of the Parties in decision SC-2/13. This decision provides the general elements that should form the basis of the Global Monitoring Plan, identifying the following underlying principles:

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 longterm 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 an effectiveness evaluation of the Stockholm Convention. Therefore decision SC-2/13 has specified a number of generic tasks to identify needs and opportunities to increase participation. These tasks include the following:
- That 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;
- That 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;
- That relevant regional centres could play a role in coordination efforts;
- That 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-2/9 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 and decision SC-2/13, 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, decision SC-2/13; and the Global Monitoring Plan and the implementation plan for the first evaluation prepared by the Preliminary Ad-hoc Technical Working Group. The later two documents will evolve over time and the reader can access the most recent versions at http://www.pops.int/documents/meetings/cop_3/meetingdocs/default.htm

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, behaviour 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 informa-

tion. 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

GEF/UNEP 2000/3. Project Decision Sheet: Regionally-Based Assessment of Persistent Toxic Substances; Project Management; and, Regional Reports

UNEP, 2001. Stockholm Convention on POPs , Text and Annexes, Interim Secretariat for the Stockholm Convention on Persistent Organic Pollutants, UNEP Chemicals, Geneva, Switzerland

UNEP, 2002. "Ridding the world from POPs" , UNEP Chemicals, Geneva, Switzerland

UNEP, 2003. Proceedings, UNEP Workshop to Develop a Global POPs Monitoring Programme to Support the Effectiveness Evaluation of the Stockholm Convention, 24-27 March 2003.

UNEP, 2004 Guidance for a Global Monitoring Programme for Persistent Organic Pollutants Ist Edition,

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. 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). The initial twelve persistent organic pollutants include the following substances or groups of substances:

- Aldrin
- Chlordane*
- Dichlorodiphenyltrichloroethane (DDT)*
- Dieldrin
- Endrin
- Heptachlor
- Hexachlorobenzene (HCB)
- Mirex
- Polychlorinated biphenyls (PCB)*
- Polychlorinated dibenzo-para-dioxins (PCDD)*
- Polychlorinated dibenzofurans (PCDF)*
- Toxaphene*

Substances marked with an asterix are mixtures of several congeners, for some of them several hundreds.

The above list is restricted to the 12 initial POPs, 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 Plan and this chapter would have to be modified accordingly.

2.2 Recommendations for POPs to be analysed

Based on recommendations from the GMP workshop in May 2003 and because it may not be necessary or even possible to analyse all individual congeners of the mixtures in the above list, the following substances are recommended for analysis (see Table 2.1). Substances in Table 2.1 include the parent POPs or selected parent congeners but also some major transformation products that are of interest for monitoring programmes to support the effectiveness evaluation.

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

For the reporting of Toxic Equivalency Factor (TEQ) (for PCDD, PCDF, and dl-PCB) it is recommended to report the concentrations of all 29 congeners and separately show the TEQ derived individually from PCDD, PCDF and dl-PCB as well as the total TEQ.

Table 2.1: Recommended analytes

Chemical	Parent POPs	Transformation products
Aldrin	Aldrin	
Chlordane	*cis*- and *trans*-chlordane	*cis*- and *trans*-nonachlor, oxychlordane
DDT	4,4'-DDT, 2,4'-DDT	4,4'-DDE, 2,4'-DDE, 4,4'-DDD, 2,4'-DDD
Dieldrin	Dieldrin	
Endrin	Endrin	
HCB	HCB	
Heptachlor	Heptachlor	heptachlorepoxide
Mirex	Mirex	
Polychlorinated biphenyls (PCB)	ÓPCB$_7$ (7 congeners: 28, 52, 101, 118, 138, 153, and 180 PCB with TEFs* (12 congeners): 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189	
Polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF)	2,3,7,8-substituted PCDD/PCDF (17 congeners)	
Toxaphene	Congeners P26, P50, P62	

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

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.

Fort the first evaluation, it is recommended to collect data for all 12 POPs (parent compounds and transformation compound as shown in Table 2.1 above) in the framework of regional implementation of the Global Monitoring Plan.

2.3 References

Web references:

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

PCB numbering and nomenclature:

PCB: http://www.epa.gov/toxteam/pcbid/table.htm

K. Ballschmiter and M. Zell (1980): Analysis of polychlorinated biphenyls (PCB) 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

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.

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 inevitable 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.

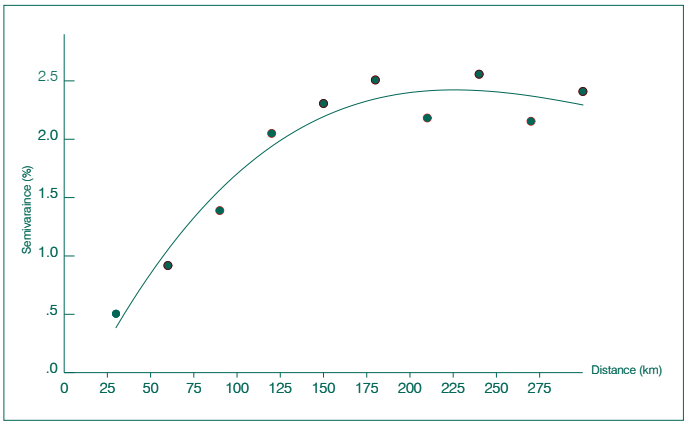


Figure 3.1: Showing an example of a variogram where the differences of concentrations between neighboring sites increases with distance up to a certain distance.

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) propose 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).

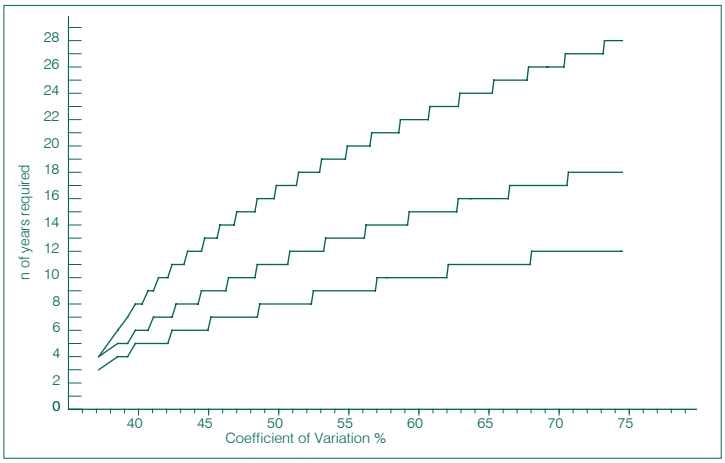


Figure 3.2: Number of years required to detect a 5 (left/above), 10 and 20% change per year respectively, at a power of 80% at a significant level of 5% applying a simple two-sided regression analysis for various magnitudes of between-years variation expressed as Coefficient of Variation (%) assuming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

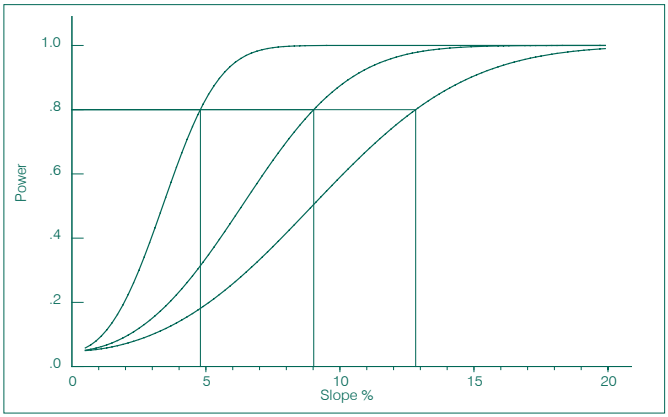


Figure 3.3: Power as a function of the minimum annual change possible to detect, after a sampling period of 12 years at a significant level of 5% applying a simple two-sided regression analysis for various magnitudes of between-years variation, expressed as Coefficient of Variation from left: 20, 40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

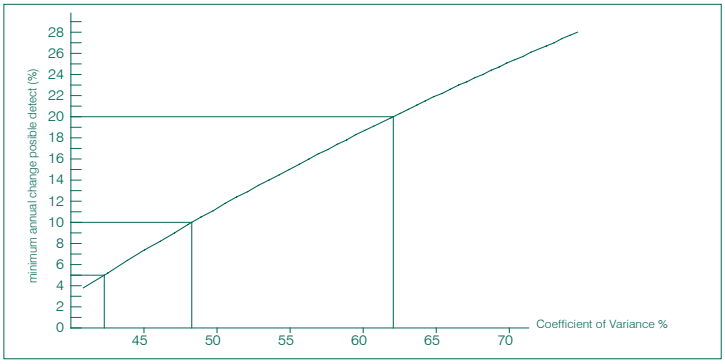


Figure 3.4: Minimum annual change possible to detect after a sampling period of 10 years at a power of 80%, a significant level of 5% applying a simple two-sided regression analysis for various magnitudes of between-years variation expressed as Coefficient of Variation (%)assuming single annual mean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

poral 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.

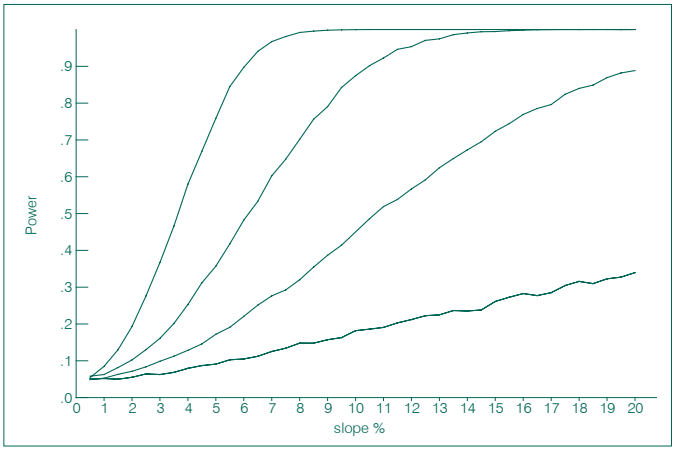


Figure 3.5: Power as a function of slope (annual change in %) at log-linear regression analysis (two-sided, á=0.05) for a sampling period of 12 years at a residual standard deviation on a log-scale of 0.20, assuming normally distributed residuals. The graphs, from left to right, represent sampling every, 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 eights 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.

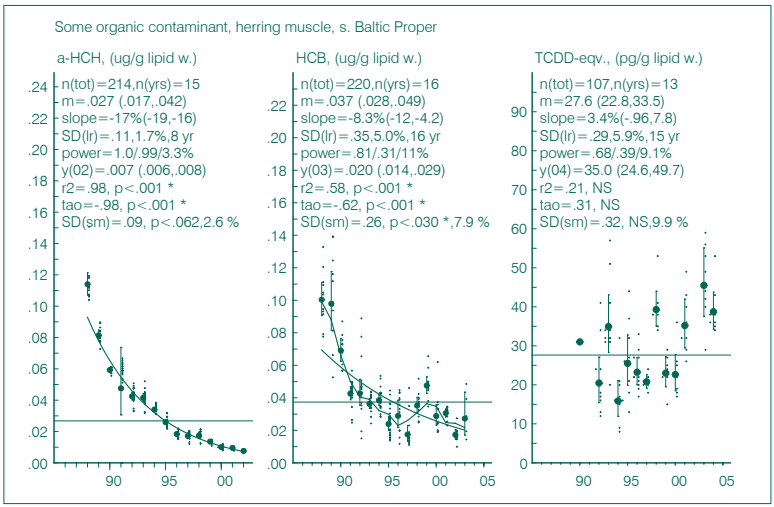


Figure 3.6: Examples of time-series; alpha-HCH, HCB and TCDD-equivalents (*µ*g/g lipid weight) in herring muscle from the southern Baltic Proper. The legend to the figure is found in Table 3.1.

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%.

r^2= The coefficient of determination (r2) 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

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 endeavour to supplement the core data with data from other media such as biota, water, soil, and sediments (SC-2/13). The present guidance is aimed at the core media for the first evaluation and the document will be revised for future evaluations. However much of the present document would apply also to the indicated supplemental media for future evaluations, but specific considerations would be needed (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 will be 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 new POPs) and may also be used for retrospective studies. Options should be developed and analyzed for inclusion in the implementation plan for the Global Monitoring Plan.

4.1 Air

4.1.1 Experimental design

Sampling sites

The objective of the ambient air sampling network is to obtain representative data for assessing time trends 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° x 20° for enhancing geographical coverage[2]. 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 need to be sufficiently remote from urban centres and industrial and other sources of POPs as to reflect concentrations typical of a large area around the site (at least 100 km radius). 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. In North America, Europe and the Arctic, some stations already exist as part of the Integrated Atmospheric Deposition Network (IADN), Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) and Arctic Monitoring and Assessment Programme (AMAP) programmes and would be used for the GMP. The East Asian POPs monitoring network, coordinated by Japan, is now producing measurements for nine Stockholm Convention POPs from several East Asian countries. In other regions, 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.

[2] Also other techniques / technologies providing comparable data could be considered.

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:

- Cumulative sampling (for 1 to 2 days every week or continuously over periods of 1 to 2 weeks) by active high volume sampling (~0.5-1 m^3/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, accessibility, buildings, platforms, towers and roads.

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 assess GMP data for a particular region using a measure of 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 TaPL3 model, which considers various degradation and transport pathways that chemicals may undergo based on their physical-chemical properties (Beyer et al., 2000). 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).

Table 4.1.1: Characteristic travel distances (CTDs, km) for air and water for selected POPs. (POPs are ranked highest to lowest in terms of the CTDs for air)

Chemical	CTD (air)	CTD (water)
Hexachlorobenzene	110 000	26 000
PCB (tetra homolog)	8900	2900
p,p'-DDE	2800	4300
Toxaphene	2500	9700

PCB (hepta homolog)	1900	2000
Dieldrin	1100	12 000
Chlordane	1000	4000
p,p'-DDT	830	3300
2378-TCDD	810	1300
OCDD	460	1900
Aldrin	100	1800

PCB-polychlorinated biphenyl; DDT – dichlorodiphenyltrichloroethane; DDE – dichlorodiphenyl-trichloroethane; TCDD – tetrachlorodibenzodioxin; OCDD – octachlorodibenzodioxin.

The resulting CTDs suggest that of the POPs listed those with important air transport pathways (the "flyers") include: hexachlorobenzene, lower molecular weight PCBs, *p,p'*-DDE and toxaphene; while those that have important water transport pathways (the "swimmers") include: hexachlorobenze, dieldrin 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. 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 (Figure 4.1.1) by identifying an air shed associated with the history of the air mass transported to a particular site.

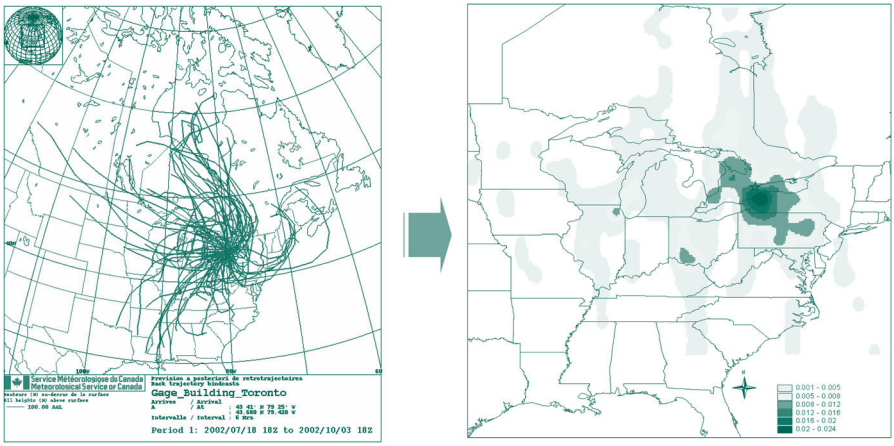

Figure 4.1.1: Example of probability density map (right panel) constructed from daily 3-day air parcel back trajectories for a time-integrated air sample.

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 fulfil 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 use of transport models for the first implementation will be limited.

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 environ-

mental 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. Some sampling networks exist. As mentioned above, active and passive samplers can be combined, offering an opportunity to create a cost-effective programme. In both active and passive sampling, POPs in particulate matter and/or the gas phase are filtered from air, separated, concentrated on a filter medium and extracted into a small amount of organic solvent for subsequent chemical analysis of POPs.

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.

High volume sampling

High volume samplers should have a size-selective inlet for collecting only those 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 subtropical 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 absorbents used need to be matched to the needs of the regional monitoring programme. Several possibilities exist which are favoured for long term measurements and should be selected by experienced experts planning a regional study:

- 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 fibre 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.

Samples could be taken for one to two days once every week or two weeks although other sampling durations may be required for detection purposes. Every fourth sample should include a field blank. This is a set of filter and absorbents that is treated exactly as the samples including placement in the sampler except no air is drawn through them. The method detection limit (MDL) is often determined by the background amounts on these blanks rather than the instrumental detection limit.

Filters and absorbents are pre-treated prior to sampling according to a methodology similar to that described in Fellin *et al*. (1996). 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). 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.

Passive sampling

Passive air sampling of POPs has undergone considerable technological development in the past decade. Early studies used semi-permeable membrane devices (SPMDs) to survey POPs over large spatial scales (Ockenden et al., 1998). Now, samplers made of polyurethane foam (PUF) disks (Shoeib and Harner, 2002) and XAD-based resin (Wania et al., 2003) have been developed and widely adopted. These samplers have been used to map the spatial variability of POPs in regional studies (Motelay-Massei et al., 2005; Gouin et al., 2005; Daly et al. 2007) and on a continental scale in North America (Shen *et al*., 2004, 2005, 2006) and Europe (Jaward *et al*., 2004 a, b). 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). A key aspect of GAPS is technology transfer and capacity building – especially in regions lacking POPs air data. Numerous regional passive sampling efforts have been initiated recently in Europe and East Asia (Jaward et al., 2004a, 2004b, 2005 – coordinated through Lancaster University, UK) and in central and eastern Europe in the recently established Central and Eastern European POPs Centre (CEEPOPsCTR) at the Masaryk University in Brno, Czech Republic– either as one-time surveys or on a continuous basis.

Passive air samplers for POPs typically rely on a sorbent with a high capacity for POPs, such as polyurethane foam (PUF) or styrene/divinylbenzene-co-polymer resin (e.g. XAD-2). For example, Shoeib and Harner (2002) use PUF disks (approximately 14 cm diameter, 1.35 cm thick), whereas Wania *et al.* (2003) employ XAD -2 resin filled into a stainless steel mesh cylinder (Figure 4.1.2). The sorbent is typically housed in protective stainless steel 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.

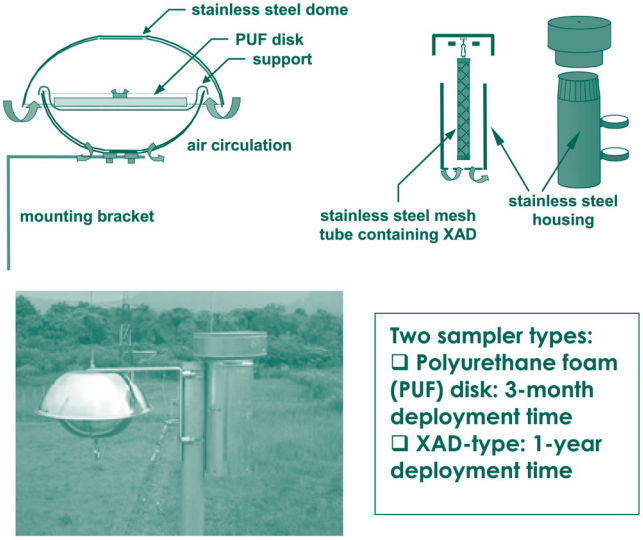

Figure: 4.1.2: Schematics and photograph of PUF-disk (left) and XAD-based passive air samplers.

Sampling rates for PUF-disk samplers are typically on the order of 3 to 4 m^3/day (Pozo et al., 2006) as so a 3-month deployment provides an equivalent sample air volume of approximately 270-360 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 ~1m/s. However, higher sampling rates have been observed at windy, coastal and mountain sites (Pozo et al., 2004, 2006).

A more precise measure of the air volume sampled may be achieved by spiking the sorbent prior to exposure with known quantities of "depuration compounds". These are isotope-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, KOA). The loss of depuration compounds over the sampling period is used to calculate the effective air sample volume (Pozo *et al.*, 2004, 2006). The air concentration is then calculated based on this air volume and the amount of chemical collected over the sampling period. When depuration 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). Otherwise, results may be reported as amount/sampler or as concentrations using a previously derived sampling rate. In this case, it is important that the greater uncertainty in the data be acknowledged.

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 depuration compounds (of similar volatility to POPs) to be used to establish site-specific sampling rates. Alternatively, PUF disk capacities can be increased by impregnating with sorptive polymers such as XAD powder. However, this would preclude the use of depuration compounds.

Sampling rates for XAD-based samplers are somewhat lower at ~0.5 m^3/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). However, this also prevents the use of depuration compounds for assessing site-specific sampling rates.

Prior to use, the sorbents such as the PUF disks and XAD-based resin, 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). 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 Considerations for time trend analysis

Chapter 3 (Statistical Considerations) outlines key considerations for conducting trend analysis on environmental data. Although, much of the analysis is presented with respect to biological data, many of the issues are applicable to air samples and should be considered when planning a sampling strategy.

Trend analysis for air data, particularly high volume 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 demonstrated periodicity that may occur seasonally or over shorter time intervals. Further, these 'harmonics' are compound- and site- specific. Digital Filtration (DF) (Hung et al., 2002) and Dynamic Harmonic Regression (DHR) (see Figure 4.1.3; Becker et al., 2006) are two techniques that have been used successfully to assess time trends.

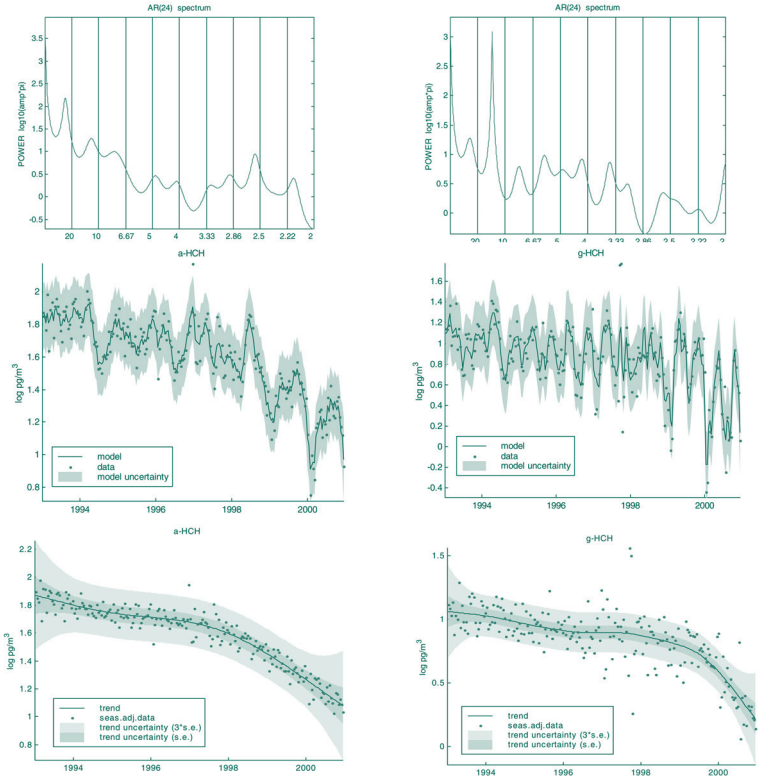

Figure 4.1.3: Example of Dynamic Harmonic Regression (DHR) for active high volume sampling data for a- and g-HCH (hexachlorocyclohexane) from 1993-2000 from Zeppelin Mountain in Svalbard, Norway. Harmonics (top panel) – harmonics are shown in biweekly periods and vary over time and with different chemicals and can provide information on chemical behaviour over short time periods (i.e. inter- or intra-seasonal patterns); Model fit (middle panel) – the measured concentrations are compared to the model fit with uncertainty to within 95% confidence levels; Trends (bottom panel) – seasonally adjusted data is used to evaluate long-term trends with uncertainty given for 95% and 90% confidence levels (Becker et al., unpublished results).

The topic of climate change and its impact on contaminant pathways introduces even more complexity for temporal trend data analysis (Macdonald et al., 2005). Correlations between air concentrations of POPs and low-frequency

climate variations (e.g. North Atlantic Oscillation - NAO, El Nino-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.

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4.2 Human milk and maternal blood as biological indicators

4.2.1 Introduction

Human milk as well as maternal blood have been used as markers of exposure of humans to certain persistent organic pollutants (POPs). Both these human sample media can 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.

Human milk

Human milk has been used on a global basis for monitoring of human body burdens of POPs for several decades. The purpose of these programmes has been to assess the body burden of contaminants in newborns, using breast milk as a tool without performing invasive sampling techniques on the newborns. An important concept in human milk studies is also that they reflect the integration of contamination at a high trophic level. Thus, human milk samples reflect the intake in different regions: the extent of contamination and different consumption habits. Furthermore, such studies are also used as general biological monitoring tools. Human milk monitoring programmes have hence been designed for assessing levels of environmental pollution by lipophilic substances in different areas within and between countries. Trends in levels and effectiveness of regulations have been evaluated by comparing these assessments with earlier investigations.

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

laboration with the International Programme on Chemical Safety (IPCS) and WHO Global Environmental Monitoring System/Food Contamination Monitoring and Assessment (GEMS/Food). In this last round of exposure studies 18 countries participated and milk samples from 62 different areas were analysed. Historical trend data exist for PCDDs/PCDFs and PCBs in some of these countries (e.g. Becher *et al.* 2002). For some countries a pilot study of concentrations of other POPs than PCBs and PCDDs/PCDFs was included in the latter study. In those studies, pooled human milk samples were used. An ongoing fourth round of exposure studies is being organised by WHO GEMS/Food, that includes all twelve POPs. The main objective of the fourth round is to produce reliable and comparable data on levels of POPs in human milk, which will serve as a basis to determine time trends in exposure to POPs. Preliminary results are available and indicate that the survey is practical, feasible and sustainable.

Human blood

The Arctic Monitoring and Assessment Programme (AMAP) have organized comprehensive human maternal blood plasma[3] 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 POPs and human health (AMAP 1998, 2004). Through this programme an international QA/QC program for blood plasma analyses has been developed, with systematic ring tests of reference standards, allowing many laboratories in the Arctic to produce reliable data on human maternal plasma as well as cord blood (CTQ, Quebec, Canada). Results show that the survey of blood is practical, feasible and sustainable.

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 under 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.

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

Historically GEMS / Food and more recently a UNEP workshop (UNEP 2003) have recognized human milk as a preferred matrix for POPs based on the fact

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

that human milk is none-invasive and can be readily obtained in quantity from lactating women whose infants are considered a vulnerable population group. There are however, three main tissues where the POP levels are normally measured in order to assess the exposure to the child: mothers 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). Recently a comprehensive study of the relationship between breast milk, maternal blood and cord blood from a group of mother and child pairs from Chukotka, Russia, has been completed (Anda *et al*, submitted). Some of the results of this paper are summarized here:

- Levels of POPs in maternal blood correlated well with the corresponding levels in human milk. 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. Maternal blood reflects both recent and past exposure and shows more rapid temporal response while milk is considered more a storage compartment. Mothers milk is the most sensitive exposure medium for the baby in terms of postnatal development.
- To extract information about the contaminant situation in a population, individual samples and individual analytical data must be obtained. Pooled samples might be considered for special, expensive analytes, such as the dioxin group, but that will provide limited information for statistical assessment of time trends.

The analytical procedures are becoming more sensitive and less expensive. Many programmes (e.g. AMAP and their QA/QC program) are assisting to develop the laboratory capacity in the new independent states of 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 a unique opportunity to increase international comparability of contaminant data by expansion of existing international GA/QC programmes in those new laboratories willing to join an educational programme for their staff and regular ring tests.

Sample size 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 popula-

tion 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 fish eating populations. Indigenous populations of the Arctic and in Africa have been shown to have different contaminant problems.

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

- Human milk and maternal blood are both good sample media for assessing POPs exposure in humans[4]. 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. It may be considered to sample both milk and blood of the same mother.
- 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 in the required time period, 2 to 4 weeks post partum.
- Blood sampling is invasive, but sampling of mothers prior to giving birth may readily be achieved. However, blood sampling may not be acceptable in certain cultures.
- Depending on local considerations, biological samples of human origin, including blood and milk, should 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. 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 is that we will only obtain information from a specific part of the population both with regard to gender and age. As for future trend studies, a careful evaluation should be done to explore alternative representative groups in a population, e.g. men (specified age groups), youth groups of both gender, school children or infants.

[4] Maternal blood plasma is the best compartment for measuring of toxic metals and elements, such as Hg, Cd and Pb. As for future screening of populations, with individual blood sampling, the metals will have increasing importance when reproductive health aspects and foetal and child developmental effects are to be addressed, but does not form part of the GMP.

- A population study must be based on sampling and analyses of individual samples; human milk or maternal blood. Pooled samples might be considered for certain contaminants, such as the dioxins which are expensive to analyze and need larger sample volumes.
- 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.
- 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). For either human milk or blood, 50 individual samples are to be collected. However, new technologies and new, certified laboratories will provide the opportunity to begin epidemiological studies with individual results on a larger scale.
- The choice of milk or blood depends very much on the practical implementation regionally or locally. 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 of Africa 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 is crucial at the sampling and analytical stages. Standardized protocols, equipment and education of field personnel as well as laboratory personnel must be implemented.

4.2.2 Objective of human monitoring within the GMP

The human monitoring within GMP will mainly aim at identifying temporal and, as appropriate, spatial trends in levels of POPs exposure in humans.

It will also assist at regional capacity building in developing countries, focused to ensure a capability to detect regional trends of POPs in humans.

4.2.3 Sampling and sample preparation methodology

Sample matrices

Human milk

The Global Monitoring Plan will use human milk as one of the two possible matrixes for biological monitoring. (See the proceedings of the GMP workshop (UNEP 2003) for more information on the recommendation for the selection of human milk as matrix suited for temporal trend studies.)

As mentioned before, human milk is an attractive medium because it is non-invasive and relatively large volumes of samples can be easily collected in a more or less standardized manner. A disadvantage is of course that only one gender constituting a limited age group is monitored. On the other hand, as the main aim of the GMP is to determine a temporal trend in exposure to POPs, the restriction of concentrating only on a small, but well defined part of the population, can be considered to be an advantage. However, in certain areas there are social or ethical difficulties to overcome in the collection of human milk samples.

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 GMP will mainly rely on data from pooled human milk samples. 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. A disadvantage with pooling is of course that information on individual variation is missed. In the Fourth WHO protocol (WHO, 2006), 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.

Additional studies can, of course, be implemented within countries to answer questions that are country specific.

Maternal blood plasma

Maternal blood plasma is used by AMAP, as the prime matrix to determine human exposure (AMAP, 2002). Although it is an invasive procedure, in some cases it may be the matrix of choice, based on local infrastructure, customs and existing activities.

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, 2006), and is based on the afore-mentioned three previous rounds of WHO coordinated studies (1987-1988, 1992-1993 and 2000-2001). This protocol will form 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 third round of the WHO exposure study (WHO 2000, Malisch and van Leeuwen 2002). This laboratory will continue to do so for the fourth round as well (WHO, 2006).

The revised WHO protocol (WHO Food Safety) 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 plasma

The protocol developed by the Centre du Toxicologie de Quebec is the standard for all blood sampling procedures in AMAP. A detailed description of sampling, storage, shipping and analytical details is presented in annex 4.

Number of samples/sampling location

Human milk

The Fourth WHO-Coordinated Survey (Malish & Moy, 2006; WHO, 2006, WHO Food Safety) requires milk samples from 50 individuals. However, current expe-

rience 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 Fourth WHO-Coordinated Survey (WHO, 2006) 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 characterised, assumptions need to be made, but these would have to be documented and form part of the information package. The Fourth WHO-Coordinated Survey (WHO, 2006) also makes provision for countries with adequate resources to submit two pooled samples, with a final volume of 500 ml for each pooled sample.

Although the Fourth WHO-Coordinated Survey (WHO, 2006) addresses countries, it may be feasible that consideration for stratification, and even sample collection, could be done on a regional level. However, the effort for this round should be focused on the participation of as many countries and regions as possible, to enable a good baseline to be set.

Maternal blood plasma

Samples from at least 50 individuals are needed. Some countries may not be able to recruit that many, and the numbers might be adjusted downwards. The final volume of the pooled blood plasma sample should still be 250 ml.

As for the milk sampling, a country should 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 characterised, assumptions need to be made, but these would have to be documented and form part of the information package. Countries with adequate resources can also submit two pooled samples of 25 sub-samples each, with a final volume of 250 ml for each pooled sample.

Again as for the milk sampling, it may be feasible that considerations for stratification, and even sample collection, could be done on a regional level. However, the effort for this round should be focused on the participation of as many countries and regions as possible, to enable a good baseline to be set.

Selection criteria for mothers

Human milk

The Fourth WHO-Coordinated Survey (WHO, 2006) lists the criteria for selection of mothers, and this should be followed as closely as possible.

Maternal blood plasma

Criteria for selection should be based on the same criteria as for milk.

Questionnaire and informed consent

Human milk

It is strongly recommended that the questionnaires developed for the Fourth round (WHO, 2006) be followed, but additional questions might be added if exposure profiles need to better characterised. 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. The protocol also allows mothers to collect samples themselves and store them in a fridge, but this might also not be possible in areas with no electricity or means of cooling. Active collection by local teams might then be the only option.

The informed consent template must also be considered by each country or region, and aligned according to local practice, custom and experience.

Maternal blood plasma

Basically, the same questionnaire and approach should be applied as for milk. Information about the invasive nature of the procedure should be included.

The informed consent template need also be considered by each country or region, and aligned according to local practice, custom and experience.

Sample handling

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.

Sample handling is particularly important for obtaining homogeneous samples of human milk for analyses and to ensure sample integrity (Lovelady *et al.,* 2002). 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.

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; Schecter *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 invasion 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.

Maternal blood plasma

Sample handling is particularly important for obtaining homogeneous samples of maternal blood plasma 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 maternal 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 maternal 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 maternal 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). Longnecker *et al*. (1999) showed that lipid adjustment for the varying levels during pregnancy allowed the best normalization of the data.

Ethics

Human milk

The Fourth WHO-Coordinated Survey (Malish & Moy, 2006; WHO, 2006) has been endorsed by the WHO Research Ethics Review Committee, but each country will also have to follow their own procedures. Any variation from the WHO 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.

Maternal blood plasma

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.

HIV/AIDS

Human milk

The Fourth WHO-Coordinated Survey (WHO, 2006) excludes mothers that are HIV/AIDS positive. In many countries though, discrimination based on HIV status is not allowed, and often the status would not be known. In addition, ethical consideration in some cases prevents enquiries as to individual's HIV status. The current questionnaire also does not refer to HIV status, and countries need

to consider this in their national context. An unknown proportion of women in many developing countries are HIV positive, but they are also part of the breastfeeding community, and their exclusion might therefore not be justifiable. Exclusions should, however, be considered when the mother is unwell, and that may therefore include conditions such as clinical hepatitis, malaria, AIDS and others, as exclusion for such a region can be justified on a scientific basis.

Although the infectivity of human milk that contains HIV may be low when ingested by babies (Newell, 1998; Iliff *et al*., 2005), human milk from regions with HIV morbidity should be considered infectious. Sample collection should take this into account and samples from areas where HIV is prevalent should be handled and labelled as such, up to and including extraction. The extracts may be considered non-infective, but any waste materials should also be considered as a bio-hazard, and must be treated as such.

Maternal blood plasma

In many countries, discrimination based on HIV infective status is not allowed, and often the status would not be known. In addition, ethical consideration in some cases prevents the HIV status from being determined. Exclusions should, however, be considered when the mother is sick, and this may therefore include conditions such as clinical hepatitis, malaria, AIDS and others, as exclusion on this basis can be justified on a scientific basis.

Since blood collection is an invasive procedure using needles, existing and well established preventative procedures should be in place to preclude any accidental infections, even by cutaneous contact with infected blood (Radecki, Abbot & Eloi, 2000). Samples from areas where HIV is prevalent should be handled and labelled as such, up to and including extraction. The extracts may be considered non-infective, but any waste materials should also be considered as a bio-hazard, and must be treated as such.

Transporting of samples

Shipping of milk and blood plasma 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.

WHO has conducted Analytical Quality Assurance assessments for human milk (WHO, 2000). Only two laboratories qualified. WHO has also carried out proficiency studies for POPs (insecticide POPs and PCB 28, 52, 101, 138, 153, 180) in human milk. Further studies are planned.

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5. ANALYTICAL METHODOLOGY

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. In case of human samples it may also be necessary to use a suitable interview form.

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.

No general recommendation can be given with respect to who should perform the sampling. For certain matrices, e.g., human blood, there is no doubt that a specialist, i.e., medical doctor or nurse, has to take the sample. In addition, for human samples, ethical considerations have to be respected. There are pros and contras 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 under established quality assurance and quality control (QA/QC) conditions. In case an external organization will be 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.

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 handing 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 a recent article (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 pigments and to separate non-polar PCB (plus p,p'-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 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.

Following fractionation on silica or Florisil final extracts are prepared in 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 PCB with TEFs differs from those used for routine ortho-PCB and OCPs in that it requires much lower detection limits (typically 10-100 times lower) because guideline limits in food products are in the low pg/kg range, the Provisional Tolerable Monthly Intake being 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 (^{13}C-surrogates for all PCDD/PCDF homo-

logue groups), enrichment on carbon to isolate planar compounds, very small final volumes (10-50 ìL) for GC-HRMS quantification is used. Methodology for PCDD/PCDF, slightly modified to include the dioxin-like PCB, developed by the US EPA, is well established and validated by numerous inter-laboratory comparisons. This methodology would be recommended for use in a global monitoring programme. Unlike the guidelines for PCB and OCPs, this very specific guidance for the extraction, isolation and quantification steps for PCDD/PCDF is recommended in order to be in compliance with ongoing programmes and compatible with results generated with these methods over the past 10 years.

5.3 POPs analysis

Since the 1960s, POPs 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). Based on the availability of commonly used instruments for the determination of POPs, three types of laboratories can be identified, as described in Table 5.1.

Table 5.1: Requirements for the instrumental analysis of POPs

Laboratory instrumentation level	Equipment	Infrastructure needs	Cost estimates (USD)	Chemicals
3	Basic sample extraction and clean-up equipment, capillary GC/ECD	Nitrogen/air conditioning/ power/personnel specifically trained to operate and troubleshoot equipment problems	Instruments: $50,000 Lab equip: $30,000 Operation: $10,000/year Personnel: 2 PY	Most PCB and all OCPs except toxaphene
2	Sample extraction and clean-up equipment, capillar GC/LRMS	Helium/air conditioning/ consistent power/ personnel specifically trained to operate and trouble-shoot equipment problems	Instruments: $150,000 Lab equip: $50,000 Operation: $20,000/year Personnel: 3 PY	Most PCB and all OCPs; toxaphene if negative chemical ionization is available

1	Sample extraction and clean-up equipment, capillary GC/HRMS specifically trained to operate and troubleshoot complicated instrumentation	Helium/air conditioning/ consistent power/high operational costs/personnel	Instruments: $400K Lab equip: $50,000 Operation: $50,000/year Personnel: 5 PY	PCDD/PCDF, all PCB, all OCPs

GC/ECD – gas chromatography/electron capture detection
GC/LRMS – gas chromatography/low resolution mass spectrometry
GC/HRMS – gas chromatography/high resolution mass spectrometry
PY – Person-year

Whereas the above table refers to estimated costs to install and run a POPs laboratory, the following indicative costs for analysis of POPs in various matrices can be given based on information provided through the UNEP/GEF project on POPs Laboratories:

- Costs for analysis of POPs pesticides (9 chemicals) range from USD 100 to USD 1,500 with a central estimate of around USD 150-200;
- Costs for analysis of indicator PCB (6-7 congeners) range from USD 90 to USD 900 with a central estimate of around USD 200;
- Costs for analysis of dioxin-like PCB (12 congeners) range from USD 140 to USD 1100 with a central estimate of around USD 750;
- Costs for analysis of PCDD/PCDF (reported as TEQ) range from USD 500 to USD 2100 with a central estimate of around USD 600-800;
- Costs for analysis of all PCDD, PCDF and PCB that contribute to the WHO-TEQ range from USD 600 to USD 1500 with a central estimate of around USD 950.

It is anticipated that improved analytical methods will be developed over the life of the Global Monitoring Plan, and it should be structured so that these improved techniques can be adopted. There is a need to improve the accuracy and lower the costs of these analyses. Emerging procedures with low environmental impact may become more widely available and accepted. It will be necessary to consider comparability as new methods are developed. This could be achieved by analysis of archived samples and direct comparison of new and old methods. Many laboratories are not currently permitted to analyze human blood and milk samples. Special training will be necessary to handle these samples, considering the danger of infectious diseases.

Quality control and quality assurance are important factors in sampling and analysis. 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 should be included in routine QA/QC. The inter-calibration exercises are an essential component in quality assurance of the results and are deemed indispensable in the implementation of a regional laboratory network. A recommendation would be that at least once a year such an inter-calibration study is performed for each matrix and 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 PCB with TEFs, quantification solely by isotope dilution HRMS is recommended and details can be found in standard operation procedures (SOPs) (e.g. EPA method 8290A, EPA method 1613).

HRMS can also be used, of course, for 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 because of wide availability, relatively low cost, and the substantial knowledge base that exists on the use of this technology for analysis of non-*ortho* and *mono-ortho* PCB and OCPs at low ng/g levels or higher in environmental matrices.

Table 5.2: General guidance on GC analysis and data reporting for POPs

GC detector	Analytes	Configuration	Advantages/disadvantages	Detection Limits [1]
Capillary GC – with Electron Capture Detection	All ortho-substituted PCB and all OCPs on the POPs list except toxaphene	30 or 60 m x 0.25 mm id. column with H_2 carrier gas. Dual column, non-polar (DB-1) and intermediate polarity columns (DB-5)	Similar response factors for most OCs. Good sensitivity for all POPs. Adequate for routine tasks. High potential for misidentification of some POPs due to co-eluting peaks	Examples: DDT/DDE ~ 1pg HCB ~0.5 pg

Quadrupole mass spectrometry in Electron Ionization (EI) mode.	All PCB and all OCPs on the POPs list except toxaphene	30 m x 0.25 mm i.d. low bleed columns with He carrier gas. Selected ion mode (SIM) for target POPs	Newer instruments (post 1997) have adequate sensitivity for routine POPs monitoring at low pg/îL concentrations. Much less potential for mis-identification than with ECD	Examples: DDT/DDE ~ 1-10 pg HCB ~1-10 pg Dieldrin ~ 25 pg Toxaphene ~ 500 pg (as technical mixture)
Quadrupole Mass spectrometry in Electron Capture Negative Ionization (ECNIMS) mode.	Toxaphene and other highly chlorinated OCPs and PCB with > 4 chlorine atoms	30 m x 0.25 mm i.d. low bleed columns with He Selected ion mode for target POPs	Comparable sensitivity to ECD in SIM mode for some POPs, in ECNIMS mode. Much less potential for misidentification than with ECD.	Examples: DDT/DDE ~ 0.1 pg HCB ~0.1 pg Dieldrin ~ 1 pg Toxaphene ~ 10 pg (as technical mixture)
Ion trap mass spectrometry using MS/MS mode	All PCB, All OCPs on the POPs list	30 m x 0.25 mm i.d. low bleed columns with He carrier gas. Same columns as quadrupole MS	Comparable sensitivity to ECD in MS/MS mode for some POPs. Much less potential for mis-identification than with ECD	Examples: DDT/DDE ~ 1 pg HCB ~1 pg Dieldrin ~ 5 pg Toxaphene ~ 100 pg (as technical mixture)
High resolution magnetic sector mass spectrometry in Electron Ionization (EI) mode	PCDD/ PCDF, all PCB, on the POPs list except toxaphene	30 m x 0.25 mm i.d. low bleed columns with He carrier gas. Selected ion mode for target POPs at 10,000 resolution	Comparable sensitivity to ECD in SIM mode. Highly reliable identification at low pg/uL levels.	Examples: DDT/DDE ~0.05 pg HCB ~0.05 pg Dieldrin ~ 0.1-0.5 pg Toxaphene ~ 10 pg (as technical mixture)

[1]The smallest amount introduced in the instrument that can be detected at signal-noise ratio (S/N) of ~10.

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 three times the noise. The lowest concentration that can quantitatively be determined (limit of quantification LOQ) is three times higher than 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 are often reported as <"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.

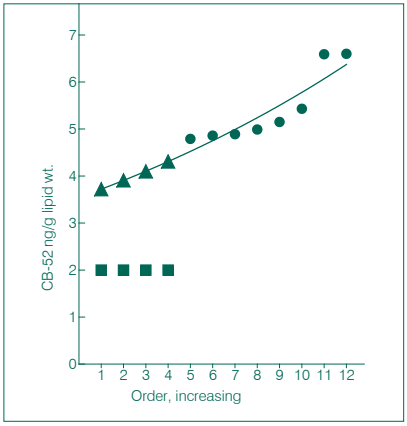

Figure 5.2: Example of substitution of concentrations reported as less than LOD, by extrapolation from regression of concentrations from the same annual sample above LOD on rank order. Log-linear regression fitted to data above LOD. Circles = concentrations above LOD, Triangles = substituted values for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

tion 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

AOAC Official Method 970.52 Organochlorine and Organophosphorous Pesticide Residue Method. General Multiresidue Method. 2005 AOAC International

AOAC Official Method 955.22 Organochlorine and Organophosphorous Pesticide Residue Method. 2005 AOAC International

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 Chromatogaphy (and ECD)

Examples: Analytical Methods for PCB

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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

EPA Method 1613: Tetra-through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, October 1994, (www.epa.gov/waterscience/methods/1613.pdf)

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)

EPA Method 8290: Polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) by high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) (EPA analytical chemistry guidance SW-846)

ISO 18073 (2004): Water quality – Determination of tetra- to octa-chlorinated dioxins and furans – Method using isotope dilution HRGC/HRMS

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Association of Official Analytical Chemists International http://www.aoac.org

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6. DATA HANDLING

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 required 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 panel[5] 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

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

of 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.

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

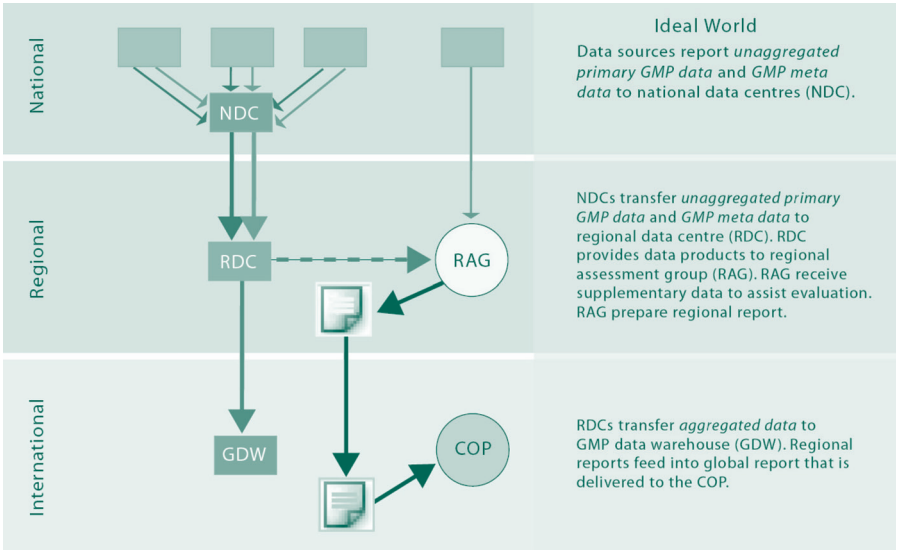
at the national level is assumed to be the responsibility of the participating countries. However, participating countries, Parties to the Convention, requiring assistance to build capacity in this respect may look to the GMP for such assistance, including exchange of experience between Parties and countries.

6.5.2 GMP data storage (compilation and archiving)

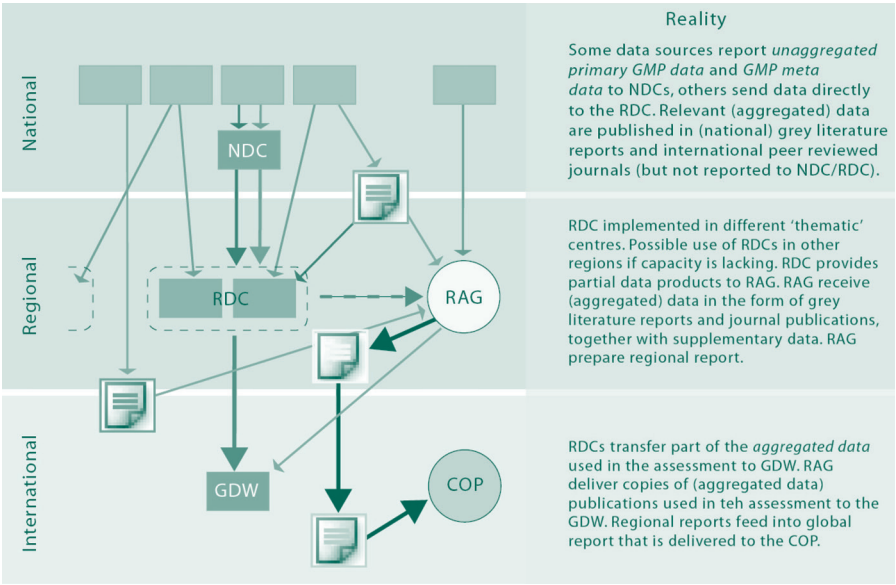
The data reporting model that is being suggested involves compiling and archiving primary GMP data within a 'regional data repository' in each of the 6 geographic regions.

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 requirement 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	Data management activities targeted only to AMAP assessment needs at present

		(ca. 20 countries, Arctic, Europe, North and South America)	
GEMS/Food	Human tissue monitoring (breast milk)		Data management activities in support of WHO breast milk surveys
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. Strategy, process and draft structure for regional monitoring reports

7.1 Introduction

In order to assist in the elaboration of the Global Monitoring Plan, it would be useful to consider the strategy, processes and structure of the first regional monitoring reports. The text in this chapter has been prepared to assist the regional organization groups (ROGs) while they are planning and setting up their information gathering activities and preparing the regional monitoring report and is based on the outcomes produced by the Technical Working Group following the decision SC-2/13. Additional information on the roles and responsibilities of the regional organisation groups can be found in the outline of the Global Monitoring Plan and implementation plan for the first evaluation[6] as adopted by the Conference of Parties to the Stockholm Convention at its third meeting.

7.2 Background

The draft structures outlined below are based upon an examination of the objectives of Article 16 of the Stockholm Convention and of the Global Monitoring Plan, together with a consideration of how other initiatives have approached similar tasks. Although a number of regional and global monitoring programmes have been established to report on the presence of POPs in the environment, there is very little previous experience of POPs monitoring designed to help evaluate the effectiveness of a legally binding international agreement. The 1998 Protocol on POPs under the Convention on Long-range Transboundary Air Pollution (which entered into force in October 2003) (UNECE 1998) contains in Article 10 a requirement to review the sufficiency and effectiveness of the obligations taking into account the effects of the deposition of POPs. The first review was completed in 2005 (UNECE, 2005).

POPs have been included in a number of monitoring programmes established to support international pollution prevention agreements, such as the periodic assessments for the Baltic Sea under the 1992 Helsinki Convention (e.g. HELCOM 1996) and the Joint Assessment and Monitoring Programme under the

[6] Drafts contained in documents UNEP/POPS/COP3/22 and UNEP/POPS/COP3/23

1992 Oslo and Paris Conventions for the Protection of the Marine Environment of the North-East Atlantic (OSPAR 2000). Monitoring to support action is also envisaged in a number of UNEP's Regional Seas Monitoring and Assessment Programmes and Action Plans with a varying degree of implementation. Examples include the Barcelona Convention's Mediterranean Action Plan; and, the Convention for the Protection and Development of the Marine Environment in the Wider Caribbean Region. Resulting assessments are published under the UNEP Regional Seas Reports and Studies Series. A North American monitoring and assessment programme which will include the current 12 Stockholm Convention POPs is being developed in Canada, Mexico and the United States (CEC 2002).

In addition, a number of global and regional assessments of the state of the environment (but not linked to pollution control agreements) have included POPs. Examples include: the various marine environment assessments undertaken by Group of Experts for the Scientific Assessment of Marine Pollution (e.g. GESAMP 2001); and the assessments undertaken for the circumpolar Arctic by the Arctic Monitoring and Assessment Programme (AMAP 2002- 4), and for Europe (EEA 1998)as well as for the Third UNEP Global Environmental Outlook (GEO-3). Other programmes have included a regional or global survey of the levels of certain POPs in particular media. Examples are the Global International Waters Assessment (GIWA 2000); the International Mussel Watch Project (e.g. Farrington and Trip, 1995; O'Connor, 1998; and Tanabe, 2000); and, surveys of certain organochlorines (including PCB, PCDD and PCDF) in food and in human milk (GEMS/FOOD 1997, GEMS/FOOD 1998, van Leeuwen and Malisch. 2002). More recently, UNEP has implemented the GEF Regionally Based Assessment of Persistent Toxic Substances (UNEP, 2003).

To identify where existing suitable monitoring data are not available, two important tools are the Regionally Based Assessment of Persistent Toxic Substances, and the fifth edition of the Master List of Actions on the Reduction and/or Elimination of releases of POPs (UNEP/POPS/INC.7/INF/15).

7.3 Outline of the strategy for the monitoring report

The Global Monitoring Plan for POPs will be comprised of regional organizational elements. Regional information gathering and preparation of the regional

monitoring report will be planned, organized, and implemented on a regional basis following an agreed framework.

Regional monitoring reports, again following an agreed format, would provide the basis for one of the elements of the Secretariat's compilation for the effectiveness evaluation; the other two being the national reports submitted by Parties pursuant to Article 15, and the non-compliance information provided pursuant to the procedures established under Article 17. Proposed organisation structure and activity flow leading to the effectiveness evaluation is outlined in Figure 7.1.

7.4 The regions

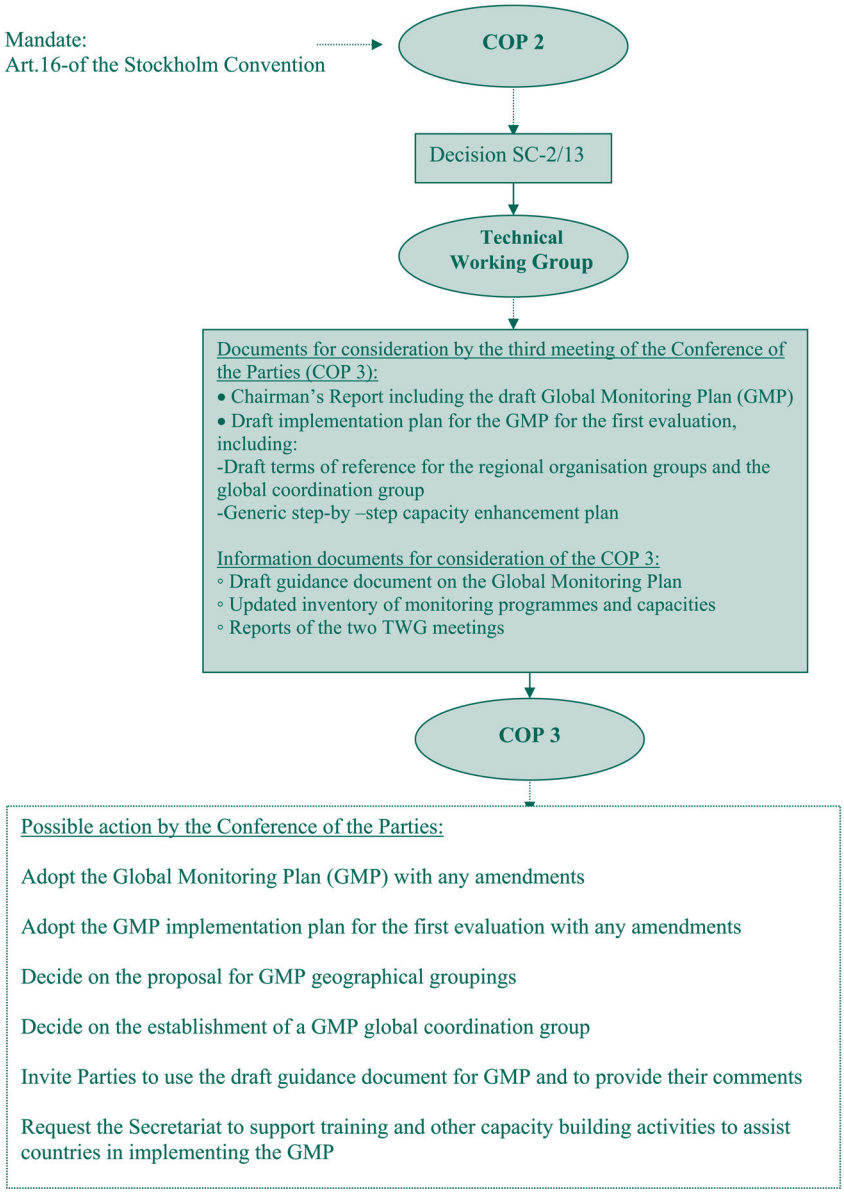
In setting up the regions, care should be taken that they provide an adequate basis for generating, collecting, reporting and presenting the data. It would seem that the best way to achieve this is to form the regions as geographical entities. This would also facilitate evaluation of regional and global environmental transport of POPs. To keep the number of regions to a manageable figure, while maintaining the geographical basis, it has been proposed to use for the purpose of the first monitoring report the following regional distribution[7]: North America; Western, Central and Eastern Europe (including the whole UN-Central and Eastern Europe region); West, South and Eastern Asia (excluding the UN-Central and Eastern Europe region); Central and South America and the Caribbean; Africa; and the region of Australia, New Zealand and the Pacific Islands. Information from the Arctic and Antarctic will be incorporated in the appropriate regions taking care to avoid overlaps between regions.

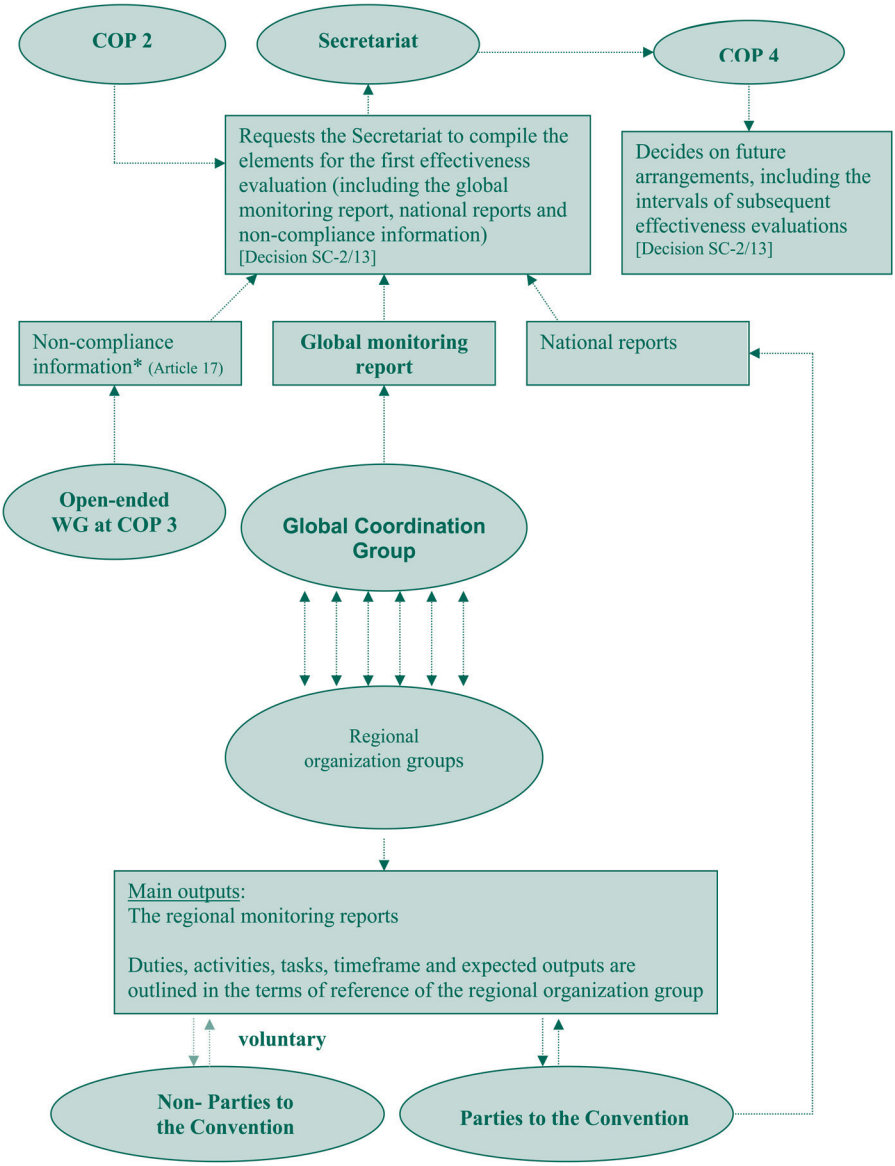
Within each region, all activities would be under the direction of a regional organization group (ROG). Some details about the roles and responsibilities of this group are given below. Sub regional and interregional arrangements that take into account linguistic, political and geophysical considerations could be introduced to further support the organization of the work.

Strategic partnerships and twinning within and between regions should be encouraged whenever possible.

[7] It should be noted that not all countries in the regions are Parties to the Stockholm Convention

Figure 7.1: Elaboration of the global monitoring report for the first effectiveness evaluation





* Any procedure that might be put in place by the COP (Decision SC-2/13).

7.5 Regional strategy for information gathering

A regional organisation group will be established in each region to be responsible for implementing the global guidance document and the Global Monitoring Plan implementation plan within that region, taking into account regional realities. The regions will be the operational units for data and information gathering, analysis, and preparing the regional monitoring report. The Secretariat and the global coordination group[8] members for each region will set up appropriate arrangements with due consideration of the existing capacities in each region for the establishment of the organization groups and networks. As far as possible, electronic communication means would be used to achieve the work. The regional organisation groups should be active as soon as possible to ensure that they can make significant progress with their work.

The duties of the regional organisation groups would include inter alia:

- Establishing its membership;
- Identifying where existing suitable monitoring data are and are not available;
- Developing a regional strategy for implementation of the Global Monitoring Plan;
- Establishing regional, sub-regional and inter-regional monitoring networks;
- Coordinating sampling and analytical arrangements;
- Ensuring compliance with protocols for QA/QC, sample collection, analytical methodologies; data archiving and accessibility; and for trend analysis methodologies;
- Maintaining the interaction with other regional organization groups and the Secretariat as appropriate;
- Developing elements to encourage capacity building;
- Preparing regional reports;
- Ensuring transparency of communication and information dissemination within the region.

In the following paragraphs the process is outlined in some detail.

The regional organisation groups, with the aid of the Secretariat, would elaborate and finalize the inventory prepared by the Secretariat in consultation with the global coordination group to identify possible contributing programmes from each region.

[8] The establishment of such a global coordination group is proposed by the Provisional Ad hoc Technical Working Group, the mandate of which expires at the third meeting of the Conference of the Parties

The regional organisation groups would apply the criteria previously established by the global coordination group to select contributing programmes in each region. The collective output of the regional organisation groups is to identify a mix of existing programmes and activities that can deliver the required data and or information without enhancement, and those that could contribute following a specified degree of capacity enhancement. The regional organisation groups will review this output in terms of the degree of regional coverage and decide upon whether and what regional capacity enhancement should be achieved for the first monitoring report. This information will provide a key input for consolidating the data and putting into place the arrangements. The exact modalities will be determined by the regional organisation groups to reflect regional conditions and will be undertaken expediently.

The regional organisation groups assisted by the Secretariat would then verify the conformity of possible regional programmes with the methodological guidance for achieving the necessary levels of comparability of data. This would be done in the context of the results from the UNEP / GEF work on laboratory capacities and performance. The regional organisation groups would prepare plans to ensure that only data and information that satisfies measures to ensure information comparability are used for the monitoring reports.

The regional organisation groups would identify how data and information from their region may be stored and accessed including the possibility of developing regional data warehouses. Further guidance is given in Chapter 6 on Data handling in this document. The possibility of using existing thematic data centres should be explored as well as the possibility of using them to serve more than one region.

The regional organisation groups, with the assistance of the Secretariat, would then establish 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 and directly from those Parties that wish to contribute nationally taking account of the work of the global coordination group to identify capacities and regional data gaps.

The regional organisation groups would (when appropriate) each set up a regional process to supplement existing core data to address regional gaps in coverage. Opportunities to establish strategic arrangements and partnerships, including with the international health sector and by developing collaborative twinning arrangements with other countries or with international monitoring organizations should be explored. Specific modalities include:

- The organization of arrangements with Parties and signatories with existing capacity and capability to provide comparable monitoring data on the core media;

- The 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; and,
- The organization of arrangements in regions without the necessary capacity to contribute to a GMP as envisaged by the Conference of the Parties. This work would be expected to require capacity building support.

The arrangements should be documented and a draft description should be available early in the process. This would also describe specific measures that are to be undertaken to secure data for the first monitoring report.

The regional organisation group would need to plan and implement, subject to availability of funding, regional capacity development that may be necessary for implementing the agreed arrangements. With regard to this the Secretariat is developing and maintaining a comprehensive regional inventory and analysis of capacities and a corresponding needs assessment with contributions from national Stockholm Convention focal points.

The final product of the regional organisation group would be an operational regional monitoring programme and a first regional monitoring report. These regional monitoring reports will form the basis for the global monitoring report for the first effectiveness evaluation.

7.6 Arrangements to address global and regional environmental transport

For the reporting on regional and global environmental transport, if the intent is to gain an understanding on the environmental movement of the listed chemicals, then a range of possibilities could be considered. These could include:

- For POPs that are mainly transported by air (the “flyers”), GMP data can be assessed using information on atmospheric transport potential (e.g. characteristic transport distances (CTD) values) and knowledge of air currents – as outlined in the Chapter 4.1.
- Back trajectory analysis (relatively simple in terms of data and infrastructure support) as outlined in Chapter 4.1. This can be extended to generate probability density maps for better interpretation of trend data with respect to advection inputs for GMP sites.
- Using regional- and global-scale models (more complex and demanding in terms of input data, although a range of models are available); GMP data can

be used to initialize models and evaluate transport pathways on a regional and trans-regional (trans-continental scale). This is a specialized and resource demanding technique that may be difficult to implement.

- As a further option the regional organisation groups could set up a small team of experts to prepare a report or reports, based upon published literature and / or the data derived from the air monitoring component of the GMP. 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 GMP.

For those chemicals for which water transport is also important (the "swimmers"), GMP data can be assessed using information on ocean currents, potential riverine inputs and considerations for air-water exchange over large water bodies. This is especially relevant for GMP data obtained in coastal areas. However, water processes may not be crucial for the original list of 12 POPs in Annexes A, B and C of the Stockholm Convention.

It is stated in paragraph 2 of Article 16 that the arrangements to be established to provide the Conference of the Parties with comparable monitoring data on the presence of the chemicals listed in the annexes should also inform the Conference of the Parties on their regional and global environmental transport. Therefore this need will also be provided for by the GMP. The guidance document describes a framework for the possible transport elements of the regional report. This guidance would include a description of:

- The discrete objectives of Article 16;
- What could be the optimal deliverables for the Conference of the Parties concerning the global and regional transport elements, bearing in mind also the budgetary concerns expressed at previous meetings of the Conference of the Parties;
- What are the data, and the analytical and assessment tools required to support the optimal deliverables;
- The present capabilities of a variety of tools developed by the scientific community that can assist in demonstrating the long-range transport of POPs. Many involve models (e.g. Shatalov, 2001; and as summarized for example in Scheringer and Wania, 2003; (OECD, 2002) and (AMAP, 1999). Regional fate and transport models can aid in the analysis of the observational data generated by the GMP (Koziol and Pudykiewicz, 2001), in particular with respect to the quantification of regional and global transport. Other less demanding methods employ back trajectory analysis (e.g. Bailey et al., 2000);

- Assessment of the existing extensive scientific research effort on the regional and global transport of POPs may be utilized;
- Concerns were expressed by the Conference of the Parties with respect to costs. Therefore it is important that in developing arrangements, new activities to service the regional monitoring report should only be undertaken if such tools can be shown to be essential for effectiveness evaluation.

Some recommendations derived from the global consultations have already been elaborated in this document. For example, the global distribution of POPs in all environmental media primarily stems from their ability to move quickly in the atmosphere with cycles of successive partitioning between air and other media. Therefore whatever may be decided upon regarding deliverables, the collection of air samples from sites not impacted by local sources and from which good meteorological information is available would be a necessity.

This was one of the primary considerations in the consultation process recommending that air should be one of the key media monitored in the POPs GMP and these needs are anticipated in those sections relating to air in the present guidance document.

A conceptual approach that may be taken by the regional organisation groups when developing their guidance is to consider the issue from the viewpoint of a “transport assessment team”.

This will help to identify the range of practical products for this component of the assessment before moving to identify the data, tools and methods required to complete the task.

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 required under Article 16. This structure is provided in annex 2 without modification.

7.7 The first monitoring report

Draft guidance for the preparation of the regional monitoring reports, including an annotated structure of the report is provided in chapter 7.8 below. In preparing the first regional monitoring report the regional organisation group should consider the following:

- The proposed baseline window could be 2003 +/- 5 years. This could be the starting point to assess changes with time.

- There could be options for providing additional information that is not obligated by the agreement e.g. trend data prior to the Convention coming into force or data from other matrices.
- There might be ownership issues for some of the data (governments vs. institutions vs. scientists). Data policy agreements should be considered.

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

7.8.1 Introduction

The objectives of Article 16 of the Convention and of the GMP.

7. 8.2 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. 8.3 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. 8.4 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);
- 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. 8.5 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. 8.6 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

For many regions, the POPs GMP will be providing the first sets of available information on levels of the chemicals in Annexes A, B and C in the environment. Therefore the detection of trends might be difficult. For the first monitoring report, those regions where data on trends may be available, a brief description of the statistical basis for the trend detection should be given. The identification of 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 first regional monitoring report, a presentation of the results according to the levels of the Annex A, B and C substances in each of the media would be sufficient and in some cases all that can be provided. This information would support the evaluation of trends in subsequent effectiveness evaluations. 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 the results will be presented in the following order:

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

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 chapter 7.6 of this guidance document.

7. 8.7 Summary of findings

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

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ANNEX 1

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 contras 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

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 ?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 ± 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 bond 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

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

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
a-chlordane	0,0050 to 10
g-chlordane	0,0030 to 10

ß-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
a-chlordane	0,0020	Non available
g-chlordane	0,0010	Non available
ß-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

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