**UNITED NATIONS
ENVIRONMENT PROGRAMME**
CHEMICALS

PROCEEDINGS

UNEP Workshop to Develop a Global POPs Monitoring Programme to Support the Effectiveness Evaluation of the Stockholm Convention

**Geneva, Switzerland
24-27 March 2003**

IOMC
INTER-ORGANIZATION PROGRAMME FOR THE SOUND MANAGEMENT OF CHEMICALS
A cooperative agreement among UNEP, ILO, FAO, WHO, UNIDO, UNITAR and OECD

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1. PREFACE

The present lack of environmental monitoring data for chemicals of concern in most parts of the world seriously impairs the analysis, evaluation and assessment of the potential threat of these substances to man and the environment. Monitoring data are needed in order to establish practical measures to evaluate and monitor the success of any implemented strategies, e.g. obligations undertaken within the scope of the Stockholm Convention on POPs. The convention also requires an effectiveness evaluation to be performed four years after entry into force. A concerted effort to harmonize and/or develop monitoring and local/regional effects data is therefore needed to provide the tools for countries to establish scientifically sound priorities for future management of chemicals, and POPs in particular.

The 6th session of the POPs Intergovernmental Negotiating Committee (POPs INC) decided to request the secretariat to begin to address the environmental monitoring and evaluation needs as described in Article 16 of the Stockholm Convention. The full text of Decision INC7/16 is attached to this report. In response to this decision UNEP Chemicals convened the present workshop to start addressing the issues in the decision. A document summarizing the main conclusions and recommendations of the workshop will be presented at 7th session of the POPs INC scheduled for mid-July 2003 for its consideration and, as appropriate, decision.

The purpose of the workshop was to provide a scientific basis for the development of guidance documents for a Global POPs Monitoring Programme that would support the effectiveness evaluation of the Stockholm Convention. Participants came from universities, existing monitoring programmes, international conventions, intergovernmental organisations and programmes, industry and environmental NGOs as well as from governments.

Discussions within working groups were supported by background documents covering the following issues:
♦ Assessment needs for effectiveness evaluation of the Stockholm Convention;
♦ Substances and Analytical Techniques;
♦ Sample Matrices, Site Selection and Sampling Techniques.
♦ Quality Assurance/Quality Control (QA/QC) and Data Treatment.
♦ Data Communication.
♦ Assessment of Global Capacity Building

Capacity building was considered as a cross cutting theme. No specific working group was set up for this; instead it was addressed in all working groups.

The workshop was supported by funding from the United States of America and the Canadian POPs Trust Fund. Their generous support is gratefully acknowledged. The organizers also wish to convey their heartfelt thanks to the co-chairs and rapporteurs of the working groups and all the experts that contributed to the successful outcome of the workshop. A special thanks goes to the meeting chair, Dr. John Buccini, Canada, who masterly managed the workshop from the very beginning through to its successful conclusion.

2. WORKSHOP PROGRAMME

Monday 24 March 2003

	Plenary Sessions Chair:	John Buccini
9.00 – 9.20	Welcome and Introduction	Jim Willis
9.20 – 9.50	Presentation of the Stockholm Convention on POPs	Bo Wahlström
9.50 – 10.10	Objectives of the workshop	Francesca Cenni
10.10 – 10.30	POPs long range transport and modeling	Frank Wania
10.30 – 11.00	**Coffee break**	
11.00 – 11.30	Effectiveness Assessment of the Stockholm Convention	David Stone
11.30 – 12.30	Effectiveness Assessment (Discussion)	All
12.30 – 13.30	**Lunch break**	
13.30 – 14.00	Effectiveness Assessment (Discussion)	All
14.00 – 14.30	Choice of substances and analytical techniques	Derek Muir
14.30 – 15.00	Site Selection, Matrices and Sampling Techniques	Kevin Jones
15.00 – 15.30	QA/QC and Data Treatment	Jacob de Boer
15.30 – 16.00	Data Communication	Noriyuki Suzuki
16.00 – 16.30	Capacity Building	Paul Whylie
16.30 – 16.45	The Global Atmosphere Watch Network: A potential Framework for Global POPs Monitoring	Len Barrie
16.30 – 18.00	Working group sessions: Assessment Substances and Analytical Techniques Matrices and Sampling QA/QC and Data Treatment Data Communication	All
18.00-18.30	Short meeting of co-chairs and rapporteurs	

	Tuesday 25 March 2003	
	Plenary Sessions Chair:	John Buccini
9.00 – 10.00	Plenary session. Co-Chairs report on the objective of each group and the subjects to be discussed	Chairs
10.00 – 10.20	**Coffee break**	
10.20 – 12.30	Working group sessions:	
	Assessment Substances and Analytical Techniques Matrices and Sampling QA/QC and Data Treatment Data Communication	
12.30 – 14.00	**Lunch break**	
14.00 – 18.00	Working group sessions:	
	Assessment Substances and Analytical Techniques Matrices and Sampling QA/QC and Data Treatment Data Communication	
18.00	Short meeting of co-chairs and rapporteurs.	

Wednesday March 26th, 2003

	Plenary Sessions Chair:	John Buccini
9.00 – 10.00	Plenary session. Short summaries of working group discussions.	Chairs
10.00 – 10.20	**Coffee break**	
10.20 – 12.30	Working group sessions:	
	Assessment	
	Substances and Analytical Techniques	
	Matrices and Sampling	
	QA/QC and Data Treatment	
	Data Communication	
12.30 – 14.00	**Lunch break**	
14.00 – 18.00	Working group sessions:	
	Assessment	
	Substances and Analytical Techniques	
	Matrices and Sampling	
	QA/QC and Data Treatment	
	Data Communication	
18.00-18.30	Short meeting of co-chairs and rapporteurs	

Thursday 27 March 2003

9.00 – 12.30	Working group sessions: Drafting of the final report.	
	Assessment	
	Substances and Analytical Techniques	
	Matrices and Sampling	
	QA/QC and Data Treatment	
	Data Communication	
12.30 – 14.00	**Lunch break**	
	Plenary Sessions Chair:	John Buccini
14.00 – 17.00	Presentation and discussion of Working Group reports:	Chairs
	Assessment	
	Substances and Analytical Techniques	
	Matrices and Sampling	
	QA/QC and Data Treatment	
	Data Communication	
	Capacity Building	
17.00 – 17.45	General discussion	All
17.45 – 18.00	Conclusions and recommendations	Bo Wahlström

WORKING GROUPS

The working groups will meet everyday during the workshop to discuss and develop the guidance on POPs environmental monitoring for the Stockholm Convention. Every group will concentrate on a subject described below:

ASSESSMENT

This working group will try to define the minimum information required by the Stockholm Convention in order to evaluate the effectiveness of the Convention itself. The discussion is based on paper n° 1.

SUBSTANCES AND ANALYTICAL TECHNIQUES.

This group will describe how to set priorities for substances in different regions and how to get comparable data on chemicals environmental levels in the environment. The discussion will be based on working paper n° 2.

SITE SELECTION, MATRICES AND SAMPLING TECHNIQUES

This group will define how to choose sites and will give a description of the relevance of each matrix. This working group will also focus the attention on recommendations concerning matrices relevant for the assessment of chemicals environmental levels. The discussion will be based on paper n° 3.

QUALITY ASSURANCE/QUALITY CONTROL (QA/QC), DATA TREATMENT

This working group will focus on necessary schemes for QA/QC procedures and on possible fields of collaboration between laboratories performing analysis of hazardous chemicals in the environment. The working group will also draw recommendations on statistics and e.g. how to treat non-detects. The discussion will be based on paper n°4.

DATA COMMUNICATION

This working group will focus on the definition of a metadata structure, standards for data communication, informative systems and GIS. The discussion will be based on paper n°5.

3. PLENARY REPORT

1. The Workshop was opened on 24 March 2003 by the chair, Dr. John Buccini, Canada. An opening statement was made by Mr. Jim Willis, Director, UNEP Chemicals. In his opening remarks Mr. Willis stressed the importance and timeliness of this workshop in view of the upcoming seventh session of the POPs Intergovernmental Negotiating Committee (INC-7).

2. Following adoption of the agenda, the Stockholm Convention on POPs was briefly described with a focus on the effectiveness evaluation in Article 16. The objectives of the workshop were described and agreed to, as well as the working group tasks. The chair stressed the need for each of the working groups to address the issue of capacity building as part of their discussions.

3. Following the background presentations, the following series of presentations were made, most of which were based on papers that had been distributed in advance of the meeting:
    *   POPs long-range transport and modelling
    *   Effectiveness assessment of the Stockholm Convention
    *   Choice of substances and analytical techniques
    *   Site selection, matrices and sampling techniques
    *   QA/QC and data treatment
    *   Data communication
    *   Capacity building, and
    *   Global Atmosphere Watch (GAW) Network
    The presentations and background papers are attached to the report

4. In the discussion that followed the assessment presentation, a series of issues were discussed and it was concluded that: a POPs Global Monitoring Programme (GMP) would mainly aim at identifying temporal and, as appropriate, spatial trends; assessments would be made on a regional basis; and a global evaluation report would be based on the regional assessments. It was stressed that the programme should strive for simplicity and while it was considered important to rely on existing programmes, the GMP would evolve over time to meet future needs. Experts from all regions underlined the need for capacity building in developing country regions.

5. The meeting agreed that the GMP would be primarily designed to follow background levels of POPs in locations far from potential sources. One expert expressed the view that urban areas should also be studied.

6. On transfer of data, a representative of WHO drew attention to the GEMS/Food Operating Program for Analytical Laboratories (OPAL), which provides laboratories and data centres with a data-handling tool, storing and manipulating raw data using a standard data structure. Individual and/or aggregate data may be transferred to regional and global data centres. Aggregate data at the global level are publicly available on the website

http://sight.who.int . The representative of WHO offered these tools for consideration in the future GMP. The meeting noted that there were also other systems available and that this needs to be looked at closely in any follow-up activity to this workshop.

7. The participants split into working groups to consider the following items:

- Effectiveness assessment of the Stockholm Convention
- Choice of substances and analytical techniques
- Site selection, matrices and sampling techniques
- QA/QC and data treatment and
- Data communication

8. The working group reports, including conclusions and recommendations, were discussed and accepted unanimously at the final plenary session and are attached to this report as Annexes 1 to 5.

9. Before closing the session, Dr. Bo Wahlström from UNEP Chemicals explained the follow-up steps to this workshop, including the presentation of a progress report to the POPs INC-7.

10. In his closing remarks the chair again stressed the importance of all participants disseminating information about the proposed GMP at the national level to prepare their delegates for the discussion at the INC-7. Following this, he closed the meeting on 27 March at 4.30 p.m.

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4. WORKING GROUP REPORTS

Working Group 1: Assessment needs for effectiveness evaluation of the Stockholm Convention

Co-Chairs: Ricardo Barra, Chile; and David Stone, Canada
Rapporteur: Henk Bouwman, South Africa

Participants: Mohammad Reza Sheikholeslami, Caspian Environment Programme; Zafar Adeel, UN University, Tokyo; Svitlana Sukhorebra, Ukraine; Sergey Dutchak European Monitoring and Evaluation Programme; Walter Jarman UNEP/Global Environmental Facility Co-ordination Office; Noriya Nakajima, Japan; Keith Bull UN Economic Commission for Europe; Gerald Moy World Health Organization; Oscar Nieto-Zapata, Colombia; Sam Adu-Kumi, Ghana; David Gee European Environmental Agency; Yasuyuki Shibata, Japan.

Background

Article 16 of the Convention requires that commencing four years after entry into force, the Conference of the Parties (COP) shall evaluate the effectiveness of the Convention. In order to do this, the COP shall, at its first meeting, begin the establishment of arrangements to provide itself with comparable environmental monitoring data on the chemicals listed in the Annexes. Reports to the COP on monitoring are required at intervals to be specified by the COP, but the Convention does not indicate how or by whom the reports will be prepared, except that it is to be a responsibility of the COP.

The charge of this group was to indicate how the gathering of data and information is to be organised and the assessment of the monitoring information to be undertaken and completed within four years of entry into force of the Convention.

Issues discussed

The purpose of the POPs Global Monitoring Programme (GMP) is to contribute towards the evaluation of the effectiveness of the Stockholm Convention as described under Article 16. In order to achieve this objective, several key elements must be considered and incorporated:
1. A sense of ownership at the national level of the monitoring programme to ensure its successful implementation; this is important to ensure involvement of the convention parties.
2. The monitoring programme must be relevant to both the implementation of the Stockholm Convention and the policies to be implemented by the Parties to comply with the Convention.
3. The sustainability of the programme must be ensured. This can be achieved through promoting simplicity of all elements, ensuring national/regional stewardship / inclusiveness, and developing capacity where needed.

It is essential that the scope of the global monitoring be clearly understood in accordance with Article 16.

1: The task to be undertaken is concerned with the gathering and assessment of information on POPs in the environment, on a regional basis when appropriate. This task may utilize information provided in the national reports and facilitate formulation of the national reports.

2: Implementation is a responsibility of the Conference of Parties and this can be achieved through participating in a regional programme.

3: Only the substances contained in Annexes A, B and C are to be considered.

4: Levels of POPs will be measured primarily in order to detect changes over time, which is essential for effectiveness evaluation. This could be given a regional focus, although it is required that a global context be included in relation to regional and global environmental transport.

5: Evaluation of the monitoring data to assess effectiveness would be assisted by the application of expert knowledge and understanding of the behaviour and movement of substances, including, for example, those changes resulting from changing economic and other activities. The activities addressed under Article 11 will therefore assist the evaluation process.

6: Monitoring for effectiveness evaluation (Article 16, paragraph 2) will not address the following: issues of compliance, preparation of dossiers for substances that may be proposed for addition to the Annexes; or, specific issues of scientific understanding. The monitoring may assist with these aspects, but this would not be reflected in the core design of the effectiveness-monitoring programme.

7: Differences in capacity within and between regions provide opportunities for regional capacity building focused to ensure a capability to detect regional trends.

8: The challenges of obtaining comparable monitoring data (e.g. harmonization; QA/QC; and the different regional capacities) suggest the need to identify the minimum information necessary to inform the COP on trends.

We also note that signatories, competent international organizations, and intergovernmental and non-governmental bodies should be encouraged to contribute relevant and acceptable information and/or to participate to the programme.

Capacity building: In order to put the GMP into regional reality, capacity building will be a crucial aspect for implementation. In keeping with the regional approach adopted for the GMP, we recommend that capacity development to service the GMP be assessed in concert with other capacity building needs assessments. Capacity building under this programme must include the following elements: a) institutional capacity, ensuring long-term sustainability of monitoring efforts; b) laboratory and technological capacity; and c) human capacity comprising professional and technical expertise.

Operational Framework for Information Gathering

In order to implement the monitoring programme as indicated in Article 16, paragraph 2(a), it was agreed that two elements of organization be required: 1 Global, 2 Regional.

Global element: It was agreed to recommend that the COP establish a subsidiary body (Global Co-ordinating Group, GCG) to oversee all of the elements in Article 16. This responsibility would include overseeing the development of a global framework for the POPs Global Monitoring Programme. Noting that Article 16, paragraph 2(a) requires monitoring arrangements to use existing monitoring programmes and their mechanisms to the extent possible, it is recommended that opportunities be sought, especially with ongoing global or major monitoring initiatives, to establish arrangements with the organizations or bodies concerned. This would be of mutual benefit, ensure harmonization and data availability, and be cost effective through minimising duplication.

The GCG, or any subgroup reporting to it, may also make recommendations on the divisions into regions, if not already decided upon by the COP. It was noted that a number of international organisations such as WHO, FAO, Economic Commissions and UNEP sharing the same regions, and the WMO have established regions. The number of regions varies between 5 and 7. The Working Group identified three considerations that could assist in deciding on the regional divisions.

1. Use existing regional structures rather then creating new divisions because they:
    a) Already possess organizational support
    b) Afford better opportunities for capacity building and technology transfer within and between regions
2. A structure with a limited number of regions would be simpler to administer. Sub-regional arrangements that take into account linguistic, political and geo-physical considerations could be introduced to further support the organisation of the work.
3. Special arrangements would be required with pre-existing programmes if these programmes have a different regional system from the one to be adopted for the POPs Global Monitoring Programme.

Regardless of the organisational structure support for developing regions such as twinning and partnerships should be encouraged.

The GCG should also be responsible for establishing a guidance document that describes *inter alia*:
• The structuring of the monitoring network
• Protocols for QA/QC, sample collection, and analytical methodologies
• Data archiving and accessibility
• Trend analysis methodologies
• The information needs and methodology of the regional and global environmental transport assessment
• The criteria for composition of the Regional Implementation Group
• Maintain interaction with all the Regional Implementation Groups
• Elements to encourage capacity building

Care is necessary to provide clear global guidance without eroding the benefits of placing the main responsibility for implementation at the regional level. Care must also be taken to ensure that the guidance document is not contradictory to other guidance documents for existing programmes that may become participants in the POPs Global Monitoring Programme.

Regional element: The regions should be the operational units for data and information gathering, analysis, and assessment. To organize the work a Regional Implementation Group (RIG) should be established in each region and be responsible for implementing the global guidance document on a regional level, taking into account regional realities. The main product of the RIG would be the regional assessment report as a feed-back to the Global Coordination Group.

Operational Framework for Preparation of the Assessment

It is envisioned that a probable format for the assessment to the COP in accordance with Article 16 will be a compendium of regional assessment reports, one for each region, together with a global overview report.

The Global Coordinating Group should include in its global guidance document a common strategy for the completion of the regional, global, and global transport assessments. It should include items such as:
•proposed draft annotated structure for each type of report
•accountabilities and responsibilities for those involved in the assessment

Information developed under Article 11, as well as information developed from other initiatives, could also be used in the regional and global assessment reports, where appropriate.

Regional assessments

The respective regions will produce substantive regional assessments by a drafting team selected by the particular region in a timely fashion. These assessments will be the main means by which the COP will be informed of the regional trends and transport of POPs in the environment.

Global assessments

The global report should be produced by a team under the purview of the GCG that should also contain individuals drawn from the writing teams of the regional assessments.

Arrangements to Address Global and Regional transport

In addition to enabling the detection of temporal trends of POPs in air, the air monitoring and modelling components will provide the information necessary to inform the COP on regional and global transport. POPs modelling continues to make significant contributions to the understanding on how POPs move through the environment. Regional fate and transport models can aid in the analysis of the

observational data generated by a GMP, in particular with respect to the quantification of regional and global transport, and the interpretation and extrapolation of time trends. Specifically, models can assist in reconciling the variability in time trends observed for different media, locations, chemical properties and time periods.

Conclusions

The combined elements of Article 16, i.e. environmental monitoring, national reporting, and compliance are an innovative feature of the Stockholm Convention. They promise to equip the COP with the ability to detect whether the environment is benefiting from the collective actions agreed upon in the Convention, and to indicate possible strengths and deficiencies in those collective actions. Together with other Articles of the Convention, they are essential to ensuring that the Convention is a living agreement that can evolve intelligently over time. In order to deliver a completed assessment four years after entry into force, it will be necessary to be able to formally establish the operational arrangements as expeditiously as possible.

Article 16, paragraph 2(a) requires that existing monitoring programmes and mechanisms should be used to the extent possible. It is recommended that opportunities for collaborative arrangements be identified as a priority. The mutual benefits will include harmonization and data availability, cost effectiveness and avoidance of duplication.

Issues for the future

It would be advantageous to test some of the elements described above before entry into force, e.g. by initiating pilot projects in developing country regions, subject to available funding.

Working Group 2: Substances and Analytical Techniques

Co-Chairs. Dr. Derek Muir, Canada and Prof Egmont Rohwer, South Africa
Rapporteur: Prof. Hian Kee Lee, Singapore

Participants: Dr. Yeru Huang, China; Dr. Alexei Konoplev, Russian Federation; Dr. Masatoshi Morita, Japan; Dr. Traoré Halimatou Koné, Mali; Mr. José Carlos Tenorio, Commission for Environmental Cooperation; Prof. Oladele Osibanjo, Nigeria, Dr. Robert Choong Kwet Yive, Mauritius; Dr. Diana Graham, USA; and Mr. Biratu Oljira Nejeri, Ethiopia

Background
This report addresses substances that will be assessed under the work of Article 16 of the Stockholm Convention on Persistent Organic Pollutants (POPs) and the analytical techniques to be adopted in the assessment. The criteria for the assessment of spatial and temporal trends of POPs concentrations at the regional level, summarized at the global level to support the effectiveness evaluation program will come from the Conference of the Parties (COP). Certain assumptions have been made about who is doing the work: laboratories will be headed by analytical chemists who have some experience in the analysis of POPs and they will have demonstrated in accordance with the recommendations of the QA/QC workgroup that they are qualified to do the work and meet data quality objectives

Objectives
The workgroup was given the following objectives:
1. Recommend the most appropriate possibilities for further prioritization between the twelve POPs in different regions of the world, since all twelve would not necessarily be of interest in every region.
2. Provide a brief overview of the main analytical techniques required to produce data for trend determinations for the POPs including all steps of the procedures, and the possibility of analyzing several components together in the same procedure.
3. Describe the possibility of using a tiered system of laboratories.
4. Comment on approaches of screening versus survey versus monitoring.
5. Comment on expected precision and accuracy required of analytical techniques.
6. Describe the capacity needed for implementation of the issues under discussion.
7.

Issues Discussed

Prioritization
Different regions have different priorities in relation to pesticides, industrial chemicals and by-products. The twelve POPs are listed in Table 1, classified by Annex and chemical class. All regions should determine background concentrations for all essential analytes at the start of the program. Some regions may already have background data that meet the requirements for this project, and some will need to develop the data. Regions can then focus analyses on the POPs that they find to be of concern.

Chemicals Under Article 16

Table 1: The Twelve POPs:

Chemical	Annex	Class
Aldrin	A	Organochlorine pesticide (OCP)
Chlordane	A	OCP
Dieldrin	A	OCP
Endrin	A	OCP
Heptachlor	A	OCP
Hexachlorobenzene (HCB)	A, C	OCP/industrial chemical/by-product
Mirex	A	OCP
Toxaphene	A	OCP
Polychlorinated Biphenyls (PCB)	A, C	Industrial chemical/by-product
DDT	B	OCP
Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF)	C	By-product

It should be noted that these are "chemical substances" and not individual analytes that would be determined in practice. Appendix 1 includes the list of recommended analytes. Generally, groups of analytes are determined together, hence reducing the number of required analyses. For example, all OCPs (except toxaphene), HCB and PCBs are analyzed together.

Analytical Methods

Sampling Requirements

Qualified personnel must be available to undertake the sampling and training may be required. Wildlife sampling will need specialized knowledge of species and collection of human samples will require training and awareness of the danger of infectious diseases. QA/QC requirements for sampling will be specified as part of project development (Workgroup on QA/QC). Currently, human samples (either blood or breast milk), wildlife samples such as birds eggs, and air samples are the matrices under consideration. All sample collection must be done in conformance with established protocols so that appropriate media are used and contamination avoided (Workgroup on Sampling). For example, high volume and passive air sampling programs need to specifically address preparation of media. Preparation of sampling media and sample containers, sample preservation, handling, shipping and storage must all be specifically addressed to ensure sample integrity.

Techniques

Numerous methods have been published over the past 30 years on the specific analytical techniques for determination of PCBs and OCPs in food and environmental matrices. Given the broad range of technical expertise for analysis of PCBs and OCPs, as evident from large international participation in interlaboratory calibration projects for these compounds, no single, detailed, step-by-step, analytical method can be recommended. Instead it is proposed that the process be "unified" using an interlaboratory calibration program. The details on the QA/QC program would be

defined by the QA/QC workgroup. Thus participants would be free to use their own methods for a given environmental matrix, although guidance would be provided as to best laboratory practices, and participation would be mandatory for laboratories identified as being in the global program.

Techniques of sample preparation, extraction, clean up, separation, detection with selective and sensitive detectors must be specified for each matrix. Table 2 describes different techniques commonly used for analysis of POPs. Gas chromatography with electron capture detection (GC/ECD) can be used to determine PCBs and OCPs on the POPs list except toxaphene. Toxaphene should be analyzed using GC/low resolution mass spectrometry (GC/LRMS) in negative chemical ionization mode. Instrumentation alone will not guarantee adequate results, but acceptable performance must be demonstrated through QA/QC performance. To avoid misidentification of analytes, confirmation techniques, such as dual column gas chromatography with GC/ECD or GC/MS are required.

To achieve required detection limits, methodologies need to have appropriate sensitivity. For example the extremely low detection limits needed for PCDD/PCDF require isotope dilution mass spectrometry, ^{13}C-isotope internal standards, enrichment on carbon to isolate planar compounds, concentration to very small final volumes analysis before GC separation and quantification by high-resolution mass spectrometry. Rapid, sensitive and inexpensive screening tools, such as in vitro cell bioassays, are available to screen environmental and biological samples for the presence of dioxin-like compounds.

It is anticipated that improved analytical methods will be developed over the life of the project. The project should be structured so that these improved techniques may be adopted. There is a need to improve the accuracy and lower the costs of these analyses. Emerging procedures with low environmental impact (microscale, immunoassay, low solvent use, etc.) may become more widely available and accepted. It will be necessary to consider comparability as new methods come along. This could be achieved by analysis of archived samples and direct comparison of new and old methods.

Many environmental laboratories are not currently allowed to analyze human blood and milk samples. Special training will be necessary to handle these samples, considering the danger of infectious diseases.

Tiered Laboratories

The project can utilize various levels of analytical capability for different types of analysis. Table 2 describes the different levels of laboratories (Tiers 1, 2 and 3) and the types of analytical capability available for determining POPs chemicals. This tier system is not the same as the 'tiers' in the QA/QC report. All laboratories participating in the project are assumed to have personnel capable of supervising sampling, data interpretation, and reporting as well as assisting in the implementation of the project. Intra-regional and inter-regional collaboration will be required to establish the network. Results of interlaboratory studies can be used to monitor performance. Each region should have at least one laboratory with Tier 1 capability, so that the region can analyze all POPs. In addition, the program may establish one laboratory for aspects of the project (e.g. preparation of performance standards) and one laboratory for each of the regions as the "reference laboratory" to provide

oversight to the quality aspects of the project. As a quality control procedure, one laboratory may analyze all or a subset of samples as a check on the precision and accuracy of analyses of other laboratories to serve as a calibration of the regional efforts. More experienced laboratories should work with less experienced groups to improve their capabilities.

Table 2: Requirements for the Instrumental Analysis of POPs

Laboratory Tier	Equipment	Infrastructure Needs	Chemicals
3	Basic sample extraction and clean-up equipment, Capillary GC/ECD	Nitrogen/air conditioning/ power/personnel specifically trained to operate and trouble-shoot equipment problems	All PCBs and all OCPs except toxaphene
2	Sample extraction and clean-up equipment, capillary GC/LRMS[a]	Helium/air conditioning/ consistent power/vacuum/ personnel specifically trained to operate and trouble-shoot equipment problems	All PCBs and all OCPs; toxaphene if negative chemical ionization is available,
1	Sample extraction and clean-up equipment, Capillary GC/HRMS[b]	Helium/air conditioning/ consistent power/high operational costs /personnel specifically trained to operate and trouble-shoot complicated instrumentation	PCDD/PCDFs, all PCBs, all OCPs except toxaphene

[a]GC/LRMS – gas chromatography/low resolution mass spectrometry
[b]GC/HRMS – gas chromatography/high resolution mass spectrometry

Detection Limits

This program's goal is to obtain environmental measurements, at locations distant from local sources; these levels are likely to be low. Therefore, it is critical that the program defines appropriate limits of detection, limits of quantification, and the selectivity of the methods. Method detection limits (MDLs) include consideration of the matrix and variability of replicate analyses. In the selection of detection limits there is a need to balance the requirement for reliable results as well as the need to achieve broad geographic coverage and avoid reporting "less thans" for a high proportion of samples.

Data Reporting

Data generated in the program must meet the data quality objectives established by the QA/QC workgroup. Data for a single chemical may be generated by various laboratories using different analytical techniques and all data that meet the quality objectives will be acceptable.

The Workgroup on Data Communication will develop reporting requirements. The objective here would be to have a record of the entire processing of the sample from preparation through to reporting concentrations that can be evaluated independently. Therefore the individual laboratories should report concentrations for analytes, blanks,

reference materials and instrument calibration results. A procedure similar to that used by QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe) for collecting inter-laboratory study data should be used. Lipid and moisture content should be reported for biota samples although concentrations should be reported on a wet weight basis.

Capacity Building

Capacity building is a critical issue for developing countries and countries with economies in transition. It should be considered at all levels in this project, including training and upgrading infrastructure and equipment. The three-tier structure for laboratories that is proposed is designed to promote opportunities for improving capacity. Relationships between more experienced and less experienced laboratories will help to increase capability. It is useful to consider existing laboratories, such as those performing pesticide residue analyses, as having the basic resources to build capacity to perform POPs analyses. The task of capacity building requires considerable resources for training, infrastructure development, equipment improvements, and sustainability. Sustainability includes continued contacts with mentors and providing adequate compensation to trained staff. Staff retention is vital to sustained capacity. Countries should consider the opportunities offered by this sort of program for capacity building, which would be beneficial for improved oversight of chemical management, food safety, promotion of trade, and meeting obligations under other environmental agreements.

Conclusions and Recommendations

Prevailing levels for all twelve POPs should be determined initially at background sites in all regions and then individual regions may establish priorities for further analysis.

Numerous methods have been published over the past 30 years on the specific analytical techniques for determination of PCBs, OCPs and dioxin/furans in food and environmental matrices, therefore, no detailed step-by-step analytical methods are recommended. Instead it is proposed that appropriate methods be selected from those already available and reliable analyses be achieved using an inter-laboratory calibration program.

A three-tiered structure for laboratories is proposed to promote opportunities for improving capacity. Each region should have at least one laboratory with Tier 1 capability, so that the region can analyze all POPs.

In order to participate in the program, all laboratories must select and validate methods capable of determining the analytes, which meet the data quality objectives and be able to demonstrate their capability. They must continue to demonstrate capability throughout the life of the program.

Organizational aspects of the Substances and Analytical Techniques topic such as provision of analytical standards, reference materials, upgrading of equipment, training and technology transfer await further definition of the intra-regional and inter-regional structure of the project.

A list of existing laboratories that could become eligible to participate in this project should be prepared for each region.

Appendix 1: Recommended Analytes for Determination of POPs[a]

Chemical	Analytes		Notes	Laboratory Tier minimum
Hexachlorobenzene	HCB	Essential		3
Chlordane (CHL)	Cis- and trans-CHL	Essential	Other octa- and nonachloro- isomers	3
	Cis- and trans-nonachlor	Essential	may be present	3
	oxychlordane	Essential	Key metabolite	3
	U83, U84, MC5, MC6	Recommended	Important chlordane components	3
Heptachlor	Heptachlor	Essential		3
	Heptachlor epoxide	Essential	Key metabolite	3
DDT	4,4'-DDE, -DDD, -DDT	Essential	DDE is important metabolite	3
	2,4'-DDE, -DDD, -DDT	Recommended		3
Mirex	Mirex	Essential		3
	Photomirex	Recommended	Important degradation product	3
Toxaphene	"total" toxaphene	Recommended	Uses technical toxaphene as a standard	2
	Congeners P26, P50, P62	Essential		2
Dieldrin	dieldrin	Essential		3
Endrin	endrin	Essential		3
Aldrin	aldrin	Essential		3
Polychlorinated Biphenyls (PCB)	(ΣPCB_7) 28/31, 52, 101/90, 118, 138, 153 and 180	Essential	Matrix dependent, biota	3
	(ΣPCB_{30}): 8/5,18,28,31,44,49,52, 95/66,87,99,101/105/132,110,118,128,146,149,151,153,138/163,156,183,187,201/157,170,180,194, 195, 206,209	Recommended	Matrix dependent, essential in air	3[b], preferably 2
	PCBs with TEFs[c] : 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 170	Essential		2[b], preferably 1
PCDD/PCDF	2,3,7,8-substituted tetra- to octachloro dibenzo-p-dioxins and dibenzofurans (17 compounds)[c]	Essential		2[b], preferably1

[a] Initial background measurements; may monitor fewer analytes after determining relative importance to regions

[b] Instrumentation dependent – low resolution MS should be used only with appropriate equipment and meeting QA/QC requirements. LRMS should not be used for PCDD/PCDFs in low level samples e.g. air

[c] reported as TEQs (dioxin toxic equivalent concentrations)

Working Group 3: Sample Matrices, Site Selection, and Sampling Techniques

Co-Chairs: Kevin Jones, UK; and Juan Colombo, Argentina
Rapporteur: Robin Law, UK

Participants: Frank Wania, Canada; Ming Wong, China; Ivan Holoubek, Czech Republic; Nageh Akeel, Jordan; Jürgen Müller, Germany; Martin Schlabach, Norway; Bo Jansson, Sweden; Paul Johnston, UK; Kiwao Kadokami, Japan; Dong Soo Lee, Republic of Korea; Nabil Bashir, Sudan; Tania Tavares, Brazil; Anna Cumanova, Republic of Moldova; Tim Brown, USA; Ann Mason, USA; Alexandre Soudine, WMO.

Background

A background paper prepared by K.C. Jones and J.L. Barber was circulated prior to the meeting and a presentation summarising the main points was given during the first plenary session. The paper is appended to the workshop report.

Objectives of the Group

The aims and objectives were clarified in plenary. The objectives and requirements for sampling under the convention are to demonstrate the effectiveness of source reduction measures. The selection of sample matrices should be chosen so as to establish the temporal trends of concentrations of POPs in media that will demonstrate the effectiveness of source/emission and exposure reduction. The Working Groups were urged to design a programme to gather the minimum data set that would allow the observation of temporal trends following implementation of the convention. The main requirements of the POPs Global Monitoring Programme (GMP) are the detection of spatial patterns and temporal trends in representative background locations, away from immediate sources, and an improved understanding of global and regional transport. Localised sources and hotspots are specifically excluded and will be addressed at the national level. Hence the specific discussions of the group focused on the selection of sample matrices for the GMP, and making recommendations on aspects of site selection and sampling techniques.

Matrix Selection

The selection of matrices focused on identifying those sample types best suited to temporal trend studies in the shorter term, and that were of global applicability. The inclusion of some of these was deemed essential to the success of the GMP. In addition, other matrices were felt to be of more use for regional and/or national studies, either because they provided supplementary information, or because their inclusion was felt to go beyond the scope of routine monitoring. Decisions about sample matrices also needed to be simple to implement, preferably utilising or building on existing programmes, and would offer opportunities for capacity building and data acquisition in developing countries. Overall, this is a considerable challenge, as for many of these compounds environmental concentrations have been reducing for some time in some regions of the world and these declines are now decreasing more

slowly than was the case in the initial phases. As a general principle, it was agreed that although samples could be pooled within countries under a regional approach, they should not be pooled across countries, as the country resolution would be lost in that event. The COP will wish to see data presented at the national level.

The matrices considered were air, water, soils and sediments, wildlife, human foodstuffs and animal feed, and human tissues. These were assessed on the basis of response time to change, homogeneity, ease of sampling, existence of ongoing programmes and networks, and as indicators of source and exposure. On this basis we recommend the inclusion within the GMP, on a global scale, of air, wildlife and human milk. It must be stressed at this point that the assessment of each matrix and its suitability for inclusion within the GMP are assigned purely from the perspectives of the requirements of the GMP and the aim of investigating temporal trends following the Convention coming into force, and *must not* be taken as applying to monitoring or research activities more generally.

Air

Air is a key and important matrix because it has a very short response time to changes in atmospheric emission and is a well-mixed medium, an entry point into food chains, and a global transport medium. Air data are required to validate atmospheric POPs transport models. Sampling networks exist, and both active and passive samplers can be used, offering an opportunity to create a cost-effective programme, at the global scale. The inclusion of air sampling within the GMP was considered to be essential, with global applicability.

Wildlife

The group felt that it was important that the GMP should include a wildlife species representative of the aquatic or terrestrial environment, such as marine mammals, bivalve molluscs or birds' eggs. No single species can be recommended worldwide. The main reason for inclusion is so that we can gain information on temporal trends on, at the least, a regional basis, in animals, which represent either top predators or important species within aquatic or terrestrial food chains. The criteria for selection were that the species be all or many of the following: widespread, with some site fidelity, well-studied with a good knowledge of their ecology and feeding habits, they should be bioaccumulators, and easily sampled. Bivalves are of particular importance as there is a large amount of data available from earlier mussel watch programmes, which can be used for comparative purposes. Bivalves are fairly ubiquitous, are found in both marine and freshwater systems and are well distributed globally, and we recommend that these be included whenever possible. Continuity of programmes is important if long-term trends are to be successfully determined. For selection of a second or alternative wildlife species, examples of other species thought to fit the set criteria were fish, marine mammals, and birds' eggs. The final choice should be made on the basis of existing and ongoing programmes, the availability of samples, and their importance in the local environment. The inclusion of at least one wildlife species reflecting the aquatic or terrestrial environment was felt to be an essential input to the assessment.

Human tissues

The inclusion of a human tissue was felt to be essential in order to include an indicator of human exposure to POPs. The sample types considered were human milk, blood, and adipose tissue, all of which have been extensively studied previously.

Human milk

There is an extensive ongoing project under WHO, with 26 countries currently participating. Historical trend data exist for a smaller group of countries. This approach allows an integrated assessment of relative food chain exposure to be undertaken, reflecting a mixture of both long-term and recent exposure, and temporal trends can be seen over relatively short periods of time. The analysis of pooled human milk samples represents an easy and cost-effective technique for comparing between countries and regions. Human milk reflects the exposure of the whole population to POPs, and its use may serve to reduce variability and increase the likelihood of observing temporal trends, as many confounding factors are removed in time trend analysis and modelling if the gender/age range is restricted. Concentrations of POPs in human milk may reflect the potential risks to human offspring. Archives of human milk samples are held in some countries, which will allow retrospective analysis of historic trends, and such archiving could be extended in the future.

There are social or ethical difficulties to overcome and sensitive communication of the resulting data will be of paramount importance if there are not to be adverse effects on the breast-feeding of children. If high concentrations are observed, follow-up studies in countries may require alternative study designs to be adopted, for instance including country-specific human milk studies and the analysis of foodstuffs.

Blood

Many national authorities already undertake contaminant analysis in blood samples, in order to characterize concentrations within their populations and to identify critically exposed groups, although probably not for all 12 POPs of the Stockholm Convention. Where these supplementary data exist, and are demonstrably of sufficiently high quality, we would recommend that they be taken into account within the global assessment. Blood sampling and handling do, however, present a relatively high risk of contact with infectious agents. Blood has a lower fat content than human milk, and larger samples will be required as a result. Also, the fat determinations used for data normalisation may be less reliable, possibly adding additional variability to the data.

Adipose tissue

This has been studied in the past, using tissue derived from surgery. In the USA a programme of this type was abandoned due to multiple problems, and in Sweden such tissues can no longer be collected. Use of this tissue was not considered further.

Of the three sample types considered, human milk was selected as the most appropriate medium, and was considered essential for the global assessment.

Water

The POPs included within the Stockholm Convention are only sparingly soluble in water, and so dissolved concentrations are very low. In addition, aquatic systems are very heterogeneous. Direct sampling of water is therefore an inappropriate choice for inclusion within the GMP. Nonetheless, inputs of POPs to water are important, and an indicator that relates to aquatic systems is desirable. It is in this context that we recommend the inclusion of aquatic wildlife on a global scale.

Sediments

As a result of their physico-chemical properties, sediments form a significant sink for POPs. However, they are extremely heterogeneous, often disturbed, and respond to changes in inputs relatively slowly. The analysis of sediment cores can provide insights into historical input profiles for persistent compounds, but sampling and analysis are complicated and this type of study is more suited to research than routine monitoring. Also, they do not yield information on very recent inputs. Sediment sampling is not a high priority for inclusion within the GMP, but is considered useful for research investigations when undertaken on a national and/or regional basis and can complement overall monitoring data.

Soil

Soil is a very heterogeneous matrix, but is potentially useful as an indicator for the terrestrial environment. The response time of soils to changes in inputs is long, and so their utility in time trend analysis is limited for the purposes of the GMP. Soils can be recommended for long-term studies over a 25 – 50 year period and as suitable materials for archiving, but are not recommended for inclusion within the GMP.

Human Foodstuffs and Animal Feed

In our strategy, we have selected human milk as a high level indicator of human exposure, and this renders the routine analysis of foodstuffs of lesser importance other than in follow-up studies, likely to be conducted on a national basis. Also, in order to assess food chain exposure via the diet, many analyses of food items need to be conducted in order to effectively assess food chain exposure, as for instance in total diet studies. These matrices present the same level of difficulty in analysis as human tissue samples and other matrices, and so there is no potential gain. Of the foodstuffs discussed, raw fish-oils may represent a useful indicator as they find their way into both human food products and animal feed. Fish-oils are produced only regionally though, and could not provide the full coverage required. For fish also, there are big regional and national differences between the species consumed and the quantities. High-fat content fish could represent useful indicator species (e.g. carp, catfish in freshwater; herring, sprat in marine waters). Butter also is not consumed in all countries, and animal fat products, such as lard, are more common in many African countries, ghee in the Middle East, India and Pakistan. Milk is produced from different animals; cows, goats, water buffalo, with different lipid contents. Eggs from domesticated fowl are available in all countries and are home-produced, and are eaten either alone or incorporated into food products. However their levels of contamination reflect their diet, which is often not representative of the local environment. We could

support the analysis of food and feed items on a national basis, with the inclusion of appropriate dietary items, in order to provide supplementary information. It was felt that useful information can be obtained from analysis of foodstuffs, but changes in dietary patterns and production techniques could alter POPs levels and exposure in ways, which are not related to overall source reductions, and so these matrices should not be regarded as essential items for inclusion within the GMP.

Therefore the essential sample types for inclusion are air, human milk, and one or more wildlife species representative of the aquatic and/or terrestrial environment. Bivalves should be included whenever possible, to reflect water quality. Higher wildlife species should be selected e.g. as indicators of top predators or because of their importance in other ways

Site Selection and Sampling Techniques

The main outlines of sampling for the various priority matrices (air, human milk, and biota) were discussed, but definitive proposals will need to be devised during the detailed design stage for the programme. Summaries of our discussions are given below:

Air

We propose that, when fully developed, the GMP contains 3 to 5 stations with active high-volume sampling in each region, so as to gather information on regional and global transport of POPs. Some of these should be sited on islands or at continental margins to gain an insight into transcontinental transport between regions. Others should be located centrally so as to obtain information on time trends of regional sources. The sites should be remote from urban centres and industrial and other sources of POPs, and should as far as possible reflect background concentrations typical of the region. Requirements for such a site include the availability of meteorological observations, the ability to perform back-trajectory analysis and station personnel who could be trained in the sampling techniques. In North America, Europe and the Arctic, such sites 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 should be used for the GMP. In other regions, use should be made of existing air quality monitoring sites that meet the appropriate site selection criteria, such as the World Meteorological Organization (WMO) Global Air Watch. At these sites, short-term 24 to 48 hours high-volume air samples should be collected at regular intervals e.g. weekly-biweekly. 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. As the sample volumes needed for reliable quantification of dioxins and furans may lead to sample breakthrough for the more volatile POPs, it may be necessary to collect duplicate samples using the same sampling equipment, each optimised for one set of determinants.

In order to gain an insight into the spatial variation of concentrations and time trends within the regions, the active sampling might be supplemented by approximately 50 to

100 sites per region at which passive sampling will be undertaken. Whereas annually averaged passive sampling is considered as an essential minimum level of effort, quarterly resolution 3month sampling periods would aid understanding of seasonal variability in transport and time trends, such as may result from monsoon periods or other seasonal phenomena. Prior to their use within the GMP, passive air samplers should be further evaluated in terms of (1) quantitative interpretability, (2) their ability to work under different climatic conditions, (3) their ability to sample POPs in both the gas-phase and the particulate phase. Air sampling will require 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.

The combination of a small number of active sampling sites supplemented by a larger number of passive sampling sites will yield a cost-effective programme. Regional availability of laboratories could influence the location of some sampling sites. We will need to encourage co-operation between countries within regions to ensure that the best sites are selected, so that they are representative of the surrounding area. Available facilities should be utilised, and where possible improved so as to enhance the capability of the network. Selected samples as opposed to extracts from both active and passive samplers should be archived for possible future analysis.

Wildlife

Bivalves

This encompasses wild mussels, oysters and clams of various species living in both marine and freshwaters. Marine samples should be representative of coastal ambient concentrations and should avoid localised hotspots. Freshwater locations should also be sited away from sources, but will also act as integrators for water transport and upstream sources. Where possible they should be based on existing programmes (e.g. mussel watch) with an appropriate coverage in each region, which we anticipate to be in the order of 100 sites. The spatial resolution of these should be adjusted in the light of human population density, land use, etc. Pooling should be of 25 – 100 individuals, selected within the centre of the size/age distributions and not at the extremes of the distribution. Concentrations should be reported on a wet weight basis, with their dry weight and lipid content as cofactors. Depuration of bivalves prior to dissection is not felt to be necessary under these conditions. Soft tissue homogenates can be stored satisfactorily at –20ºC, and can also be archived in this way. Extraction should be conducted close to the sampling locations wherever possible, and development of laboratory facilities for this purpose represents a capacity-building objective. The recommended frequency of sampling is annually, one month prior to spawning so as to maximise the POPs concentrations determined. Selected samples should be archived for possible future analysis.

Fish

Freshwater and marine fish represent ambient POPs concentrations in water and, primarily, in their diet. Relatively high-fat fish (> 10% lipid content) is preferred, for example herring as a pelagic fish. The selection of an appropriate species will require that advice be taken on the local fish stock structures, migratory behaviour of fish, and other factors. The recommended sampling frequency is annually, although in the first year more detailed sampling may be needed in order to characterise individual variability. The selection of fish samples for time trend detection, in terms of age-stratified sampling, sample size, and the impact of pooling strategies on the power of statistical analysis have been well studied within other monitoring programmes such as the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR Convention) programmes, and detailed advice is available from International Council for the Exploration of the Sea (ICES). Strict protocols will need to be established for pooling, homogenisation, freezing for storage, extraction and analysis, so as to maximise the time trend information, which can be produced. Representative fish will need to be selected from freshwater, both from rivers and lakes. Selected samples should be archived for possible future analysis.

Birds' eggs and Marine Mammals

The GMP should build on existing programmes as far as possible. Species selection should be related to feeding habits, non-migratory nature, and other characteristics. Work to date has concentrated primarily on seabirds (e.g. gulls, guillemots) and this is a desirable feature as outlined above. However, there is also an opportunity to select species that would also focus attention on terrestrial food chains, which are not represented by other matrices. In some studies owls and falcons have been selected for this purpose, but other species may be appropriate. Sampling frequency should be annual. Detailed guidance on the use of birds' eggs for temporal trend monitoring is available from ongoing programmes, in Sweden and the Great Lakes area, for example. Ringed seal are studied in the Arctic. Selected samples should be archived for possible future analysis.

Human Milk

The concentrations of POPs in human milk reflect the full environmental exposure of women, including all aspects of their life. Human milk, with its high lipid content, is an ideal matrix for tracking this exposure, and so represents an ideal matrix for inclusion within the GMP. Within the WHO Global Environmental Monitoring System (GEMS) there is an existing programme with which GMP can align, and this has established detailed protocols for sample collection, data handling and dissemination that could usefully be adopted. The suggested frequency of sampling is 3 to 5 years for countries or regions, which are just beginning to implement controls for POPs, and every 5 years for countries with established controls. Under the WHO programme, each participating country submits at least 2 samples of milk, each representing a pool of milk from at least 10 women, who are nursing their first child. Sampling should begin when lactation is fully established, after 2 – 4 weeks. Within the GMP, samples will need to be selected so that they reflect, to the greatest degree possible, the cultural and exposure diversity within each region. These pooled samples

are intended to represent an average concentration from diverse populations, however additional studies could be implemented within countries in order to assess the success of the Stockholm Convention. This could be used as an aid with which to promote capacity building within countries, and also to answer questions that are country specific. WHO and other experts could perhaps be used as a training resource. With regard to sample collection, sample handling and archiving, the current WHO protocols could be followed in their entirety. It should be noted that individual countries are, of course, free to increase the numbers of samples they submit for analysis under the programme, or to pursue their own programmes, to use human tissues to gain information on variable exposures in the population due to diet, ethnic origin, age etc.

As mentioned above, there are social and ethical considerations to be taken into account when recruiting women and when taking and analysing human milk samples. Sampling should not interfere with breast-feeding, or hinder WHO's goal of increasing the practice of breast-feeding globally. In addition, individual countries may have specific requirements, which must be adhered to. Again, WHO experience is invaluable in this respect.

Note for the Future

Within this meeting we concentrated our discussions on the twelve POPs currently defined within the Stockholm Convention. It should be noted though that not all future candidate POPs may be lipid soluble, and that as we develop sample archiving facilities it should be borne in mind that we may need to store a wider range of tissues.

Capacity building

We must support existing facilities on a national basis, and aim to develop improved facilities at the regional level. Training on sampling techniques, and the adoption and validation of appropriate sampling, sample handling, storage and transport methods will be facilitated by contacts between expert laboratories and those whose capacity is to be developed, and the provision of in-service training. Assistance with study design and implementation should also be made available.

Conclusions and recommendations

Proposed Sample matrices for the POPs GMP

The Working group proposed that the following matrices be considered:
- Air
- Bivalves
- Wildlife species
- Human milk

Recommendations on sample frequency etc

Air

The GMP should contain a limited number of active sampling sites per region, using existing stations to the extent possible. Others may be established at existing stations (e.g. WMO locations). Samples may be taken every 2 weeks.

In addition, passive sampling should be considered. Passive stations may be set up in each region, linked to national weather and/or air sampling locations. An annual sample from each station would be considered a minimum, while 3 to 4 samples per year would be preferred.

Bivalves

Bivalves are suggested as an aquatic 'sentinel' that could be used for spatial mapping and trends. Species might be freshwater and/or coastal, as appropriate for the region. They should be sampled to provide a bulk sample from each location every year. The site selection could be based on the Global Mussel Watch or on national programmes.

Other biota

These might be sampled to provide regional quality indicators for the marine/terrestrial environment, using sensitive species that are responsive indicators to time trends. The species should be regionally selected (from e.g. bird eggs, fish or marine mammals), based on a number of recommended criteria. The criteria should be set to aid in trend monitoring (e.g. pooling; choice of age etc sampled). Temporal trends should be determined by analysis e.g. every 3-5 years.

Human milk

The WHO approach may be adopted provided that it fulfils the requirements of the effectiveness evaluation of the SC. Pooled samples from individual countries may be used. The number of samples may vary with size of country. The results may trigger further studies at national level, concerning sources and exposure pathways.

Additional comments

The need for considerable supporting analyses e.g. duplicates/blanks/ QA/QC etc may substantially increase number of samples. A statistical evaluation on the number of samples and sampling frequencies should be performed before taking decisions on the details of the programme. The most demanding analytical requirements would be the determination of PCDD/Fs in background air, because of the very low concentrations of these compounds present in the background global atmosphere.

Working Group 4: Quality Assurance/Quality Control and Data Treatment

Co-Chairs: Mrs. Dr. S. Canna Michaelidou, Cyprus; and Dr. R. Malisch, Germany
Rapporteur: Dr. J. de Boer, the Netherlands

Participants: Ms. A. Aleksandryan, Armenia; Prof. W. Aalbersberg, Fiji; Dr. P. Kishore Seth, India; Dr. D. Robinson, Jamaica; Mrs. Dr. E.C. Santiago, the Philippines; Prof. Dr. P.H. Viet, Vietnam; Dr. P. Tia, Zimbabwe; Dr. K. Kawata, japan; and Prof. G. Maghuin-Rogister, Belgium.

Introduction

Quality assurance/quality control (QA/QC) is a system to ensure that the data generated by a laboratory are of the highest quality possible and thereby acceptable to all parties. This report aims at providing the conceptual basis and the principles for dealing with the issues of QA/QC of the POPs Global Monitoring Programme (GMP). The rationale for providing such a framework rather than prescribing detailed quantitative requirements is based on the following:
a) Describing analytical criteria in detail is a very comprehensive task. Different groups are dealing with this issue (e.g. at EU and international bodies) and often with slightly different conclusions that require much time to harmonize. The QA/QC criteria to be applied for the GMP have to be in line with internationally accepted criteria and adapted to changes such as technological developments.
b) The GMP will be a dynamic process in terms of the range of concentrations of persistent organic pollutants (POPs) and the matrices to be analyzed. The QA/QC system has to be adapted and optimized according to the actual state of the program.

Therefore, under the Stockholm Convention it is recommended that a mechanism be established to set detailed QA/QC criteria and coordinate the QA/QC system.

Issues discussed

Operational considerations

Participating institutions

The main target of the monitoring program is to evaluate the effectiveness of the Convention globally. To this effect, reliable and comparable data need to be generated according to pre-set criteria. The structure of the analytical program has been chosen to ensure high quality data allowing a meaningful analysis of trends while at the same time involving as many Convention parties as possible.

It is recommended to set up a system of responsibility with:
   i)   Reference laboratory(ies) in each region accredited to carry out analyses and to perform confirmatory analyses if necessary. These laboratories will also have a mandate to provide guidance to the other

   laboratories on methods and QA/QC aspects. A reference laboratory might be designated for a specific matrix or analyte only, or for all matrices and analytes involved.

ii) Monitoring laboratories to carry out routine analyses. Preferably, laboratories should be accredited. In addition, laboratories with an appropriate QA system that can meet the pre-set criteria can participate and gradually, through capacity building activities, be supported to achieve accreditation.

iii) Institutions with a capacity and a capability for sample collection, which meet the quality criteria for sampling.

An inventory of potential participating laboratories needs to be compiled and assessed at an early stage of the program.

Performance assessment

All laboratories involved will be selected according to their ability to meet a set of quality criteria. Laboratories accredited for the analysis of POPs will be accepted and do not need further audits, as they are already being externally audited on a regular basis. Laboratories, having a QA/QC system, but no POPs accreditation, will be evaluated by an expert group that will identify those with sufficient quality to enter the programme and the potential to obtain accreditation within a reasonable period of time. Another key criterion for laboratory acceptance should be the ability to achieve minimal, globally accepted detection limits, accuracy and precision. Detection limits should in general be at ca. 20% or less of the levels of interest. Typical acceptable values for other QA parameters are given in Annex I (EU 2002a,b).

Methods

The laboratories should use validated (IUPAC, 2002), or internationally recognised (e.g. ISO) methods, fit for the purpose of this programme, for example matrix analysed and concentration range. A more detailed description is found in the report of the Working Group 2, Substances and Analytical Techniques

Components of QA/QC procedures

Key elements in QA/QC are the use of reference materials and quality charts, participation in interlaboratory studies, and the use of guidelines for sampling and analysis.

Reference materials

Certified reference materials (CRMs) are available for a number of POPs (see QA/QC background document). The use of CRMs, a key component of QA/QC procedures, is required where available.

For a number of POPs and matrices however, CRMs are not available. It is therefore recommended that UNEP/Stockholm Convention Secretariat establish ways to make them available, either by contacting dedicated organisations, or through specific projects under the GMP programme.

The use of laboratory reference materials (LRMs) and the preparation of quality charts will be of utmost importance. Thus, the central preparation of a large batch of LRMs is recommended.

Interlaboratory studies

It is proposed to centrally organise proficiency tests for all the POP/matrix combinations, at least on an annual basis. Such an annual assessment is mandatory for accredited laboratories. This could be a scheme especially organised for this GMP programme or part of existing interlaboratory/proficiency testing schemes. However, for matrices such as human samples or air, there may be only very limited possibilities. For these matrices, preference should be given to the coordination of the interlaboratory studies under the GMP programme.

In addition, it is recommended that laboratories regularly share samples for analysis, e.g. one sample per batch at a monitoring laboratory could be analysed by the reference laboratory.

In the absence of CRMs and interlaboratory studies, the analytical performance should be demonstrated by regular blank analysis, spiked samples, duplicates, and confirmatory analyses (IUPAC, 2002).

Other QA components

- Sampling protocols (method, number, size and representativeness)
- Limit of detection/quantification
- Blanks
- Recoveries
- Duplicates
- Calibration
- Surrogate and internal standards
- QA of co-factors (such as lipid, organic carbon and moisture content)
- Confirmatory tests (e.g. use of second GC column or other detection system)

Data acceptance

Prior to being included into the database, laboratory results should have passed all the quality criteria. Therefore, data should be scrutinised by the laboratory generating them in the first place. Then the data, confidence intervals and all supporting information on QA sampling and methods should be evaluated by a regional quality review panel.

A system of flagging should be developed for data that are generally acceptable but do not fulfil all quality criteria, and also for those data that are between the limit of detection and the limit of quantification.

Non-detects should be reported as less than the detection limit (the value of which has to be reported). A system, based on literature, needs to be developed to deal with non-detects in calculations. For TEQ calculation in the case of dioxin 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, 57th meeting, WHO Food Additives Series 48).

The definition of the detection limit and the use of units of reporting within the GMP programme need to be harmonised.

Trend identification

Laboratories are encouraged to achieve results, which are as accurate as possible, by using CRMs, LRMs, participating in interlaboratory studies, etc.

The identification of trends will require that statistical evaluation be thoroughly carried out on the programme design as a whole to ensure that it is powerful enough to detect trends of interest including establishing the target accuracy of the analysis.

It should be kept in mind that the statistical power is likely to be reduced when data of more laboratories are used. Given the expected variability in results of interlaboratory studies, it is recommended to record site-specific trends in POP concentrations based on results of single laboratories. However, more advanced statistical approaches may be able to identify regional trends with sufficient precision, based on results of more laboratories.

Capacity building

Capacity building will particularly benefit from a good networking system both on an intra-regional and an inter-regional scale. This networking system will draw on national and regional laboratories, reference laboratories, and external experts.

Successful capacity building can only be achieved by adopting a holistic approach. This would include training workshops, both on a global scale and dedicated workshops on specific topics, as well as advice on literature, guidelines, standards, methods, reference materials, stepwise designed inter-laboratory studies, and

exchange programmes. The QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe) programme, being an ongoing performance improvement programme applying such a holistic approach, may serve as an appropriate model (see QA/QC background document).

It is recognised in some regions there is a need to develop infrastructure for POPs analysis. This could either be promoted through this project or through other programs.

Conclusions and recommendations

1. An effective quality assurance system should be established for the whole program. This system will provide one set of criteria to be used at all levels.
2. Under the Conference of the Parties a mechanism should be established to coordinate QA/QC aspects, and to set detailed criteria in accordance with the range of POPs concentrations of interest to be specified for the different matrices.
3. It is recommended to set up a system of responsibility including at least one reference laboratory per region, monitoring laboratories, and institutions responsible for sample collection.
4. An inventory of potential participating laboratories needs to be compiled and assessed, with the final selection carried out by a group of experts based on a performance assessment.
5. The laboratories should use validated or internationally recognised methods, fit for the purpose of this programme, and demonstrate this ability for the matrix to be analysed in the concentration range of interest.
6. A mechanism should be established to make certified reference materials and laboratory reference materials available from a central source.
7. A proficiency testing system should be organised on an annual basis for all POP/matrix combinations involved in the program.
8. In each region, a review panel should be installed to evaluate the data prior to acceptance.
9. A statistical evaluation is necessary before identifying trends beyond the site-specific level.
10. A holistic, ongoing capacity building plan should be established based on effective networking within and between the regions.

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Annex I

Examples from EU, 2002a (applicable for POPs analysis in food)

Trueness of a quantitative method.
In the case of repeated analysis of a CRM, the guideline ranges for the deviation of the experimentally determined recovery corrected mean mass fraction from the certified value are as follows:

Mass fraction	Range
< 1 μg/kg	-50% to + 20%
> 1 μg/kg to 10 μg/kg	-30% to + 10%
> 10 μg/kg	-20% to + 10%

When no such CRMs are available, it is acceptable that trueness of measurements is assessed through recovery of additions of known amounts of the analytes to a blank matrix. Data corrected with the mean recovery are only acceptable when they fall within the ranges shown in the table above.

Precision of quantitative methods.
The interlaboratory coefficient of variation (CV) for the repeated analysis of a reference or fortified material, under reproducibility conditions, shall not exceed the level calculated by the Horwitz equation. The equation is: $CV = 2^{(1-0.5\log C)}$,
where C is the mass fraction expressed as a power (exponent) of 10. Examples are shown in the following table.

Mass fraction	Reproducibility CV (%)
1 μg/kg	(*)
10 μg/kg	(*)
100μg/kg	23
1 000 μg/kg	16

(*) For mass fractions lower than 100 μg/kg, the application of the Horwitz equation gives unacceptably high values. Therefore, the CVs for concentrations lower than 100 μg/kg shall be as low as possible.
For analyses carried out under repeatability conditions, the intra-laboratory CV would typically be between one-half and two-thirds of the above values. For analyses carried out under within-laboratory reproducibility conditions, the within-laboratory CV shall not be greater than the reproducibility CV.

Examples from EU, 2002b (applicable for dioxin analysis in food):
Laboratories shall demonstrate the performance of a method in the range of the level of interest, e.g. 0.5x, 1x, and 2x the level of interest with an acceptable CV for repeated analysis. The following criteria have to be complied with on total TEQ value:

	Confirmatory methods
Trueness	-20 - + 20%
CV	< 15 %

Working Group 5: Data Communication

Co-chairs: Dr Noriyuki Suzuki, Japan; and Ms Janet Pawlak, Denmark
Rapporteur: Dr Simon Wilson, Norway

Participants: Ms Constance Haaser, United States of America; Dr Fouad Abousamra, Greece; Dr John Edmonds, Japan; Mr Larry LaFleur, United States of America; Dr Simon J. Buckland, New Zealand; Dr Muhammed Omotola, UNEP Chemicals; and Prof. Bo Jansson, Sweden.

Background

Article 16 of the Stockholm Convention describes measures that should be implemented for *evaluating the effectiveness* of the Convention by the Conference of the Parties (COP). Specifically, it identifies the availability of *comparable monitoring data* as a prerequisite for such an evaluation, and preliminary work has been undertaken to establish a global monitoring programme to generate relevant data.

The purpose of this Working Group is to develop a data communications strategy, including the collation of monitoring data and the establishment of central data/information compilation facilities, to facilitate the evaluation of the effectiveness of the Stockholm Convention.

Issues Discussed

The group identified a holistic approach to manage the flow of data from the data sources to the primary users of the data, mainly the COP. At each step in this data flow, relevant solutions were identified to address data management aspects that are pertinent.

A vision for data flow from Data Sources to the COP

The main components in the envisaged data flow are those from (a variety of) data sources to the data storage and processing facilities and from the data storage facilities through a regional assessment process to the global effectiveness evaluation and the ultimate client, the COP. This flow is illustrated in Figure 1.
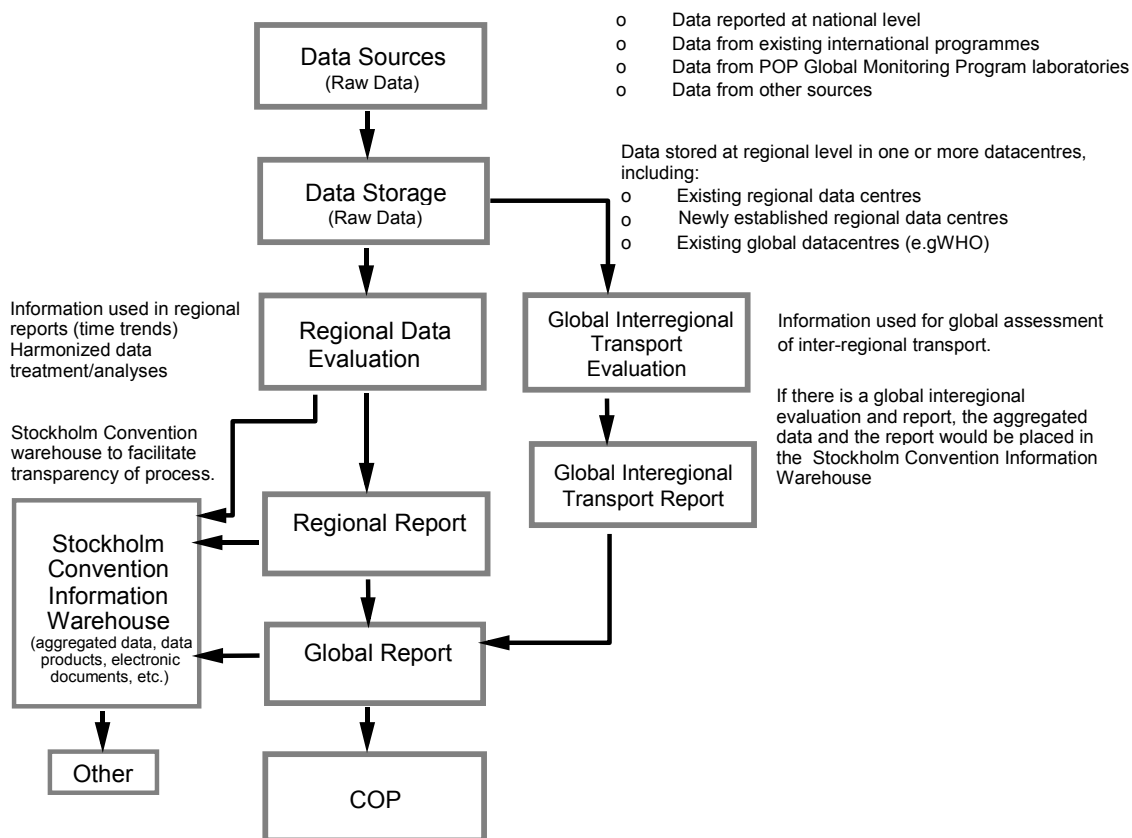
A list of definitions of some of the terms used in this document is attached as Annex 1. This data flow can be described as follows:

Data Sources: Data for the Global Monitoring Programme will primarily be based on national or sub-regional monitoring, however, regional and international data sets may also be included. As it is not yet clear exactly what mechanisms and procedures will be involved in data reporting, three generic groups of data supplier have been identified:

(1) national governments, directly providing all relevant data from their national monitoring programmes;

(2) a nominated body associated with the POPs Global Monitoring Programme activities (e.g., a regional or international organization holding relevant national, regional and/or international data collections, possibly including one (or more) designated POPs Global Monitoring Programme laboratory(ies));

(3) other sources, for example, individual scientists/researchers, independent laboratories, industry, NGOs, etc. Several of these are sources of data that might be desirable to include (historical data to extend time trends backwards for the period prior to the establishment of the POPs Global Monitoring Programme, modellers potentially contributing information on inter-regional transport, etc.).

Data Storage: The main storage and processing of raw data (i.e., detailed sample measurement data) should be organized at the regional level. The facilities for handling the raw data arising from the Global Monitoring Programme data are envisaged to be a collection of regional databases that are capable of storing data from the global monitoring programme <u>AND</u> making these data available in an appropriate manner for use in the effectiveness evaluations. The individual components within this data handling system are envisaged to include:

(1) Existing data centres currently handling regional and/or global data sets, some of which can be 'tagged' for use in the Stockholm Convention effectiveness evaluation – tagging data and making use of existing systems can be expected to be much less resource demanding than establishing new systems to do the same work.

(2) New regional data centres that may need to be established. The ultimate objective will be to ensure the necessary capability and capacity in all regions.

Evaluation Process: The regional data centres are intended to support a regional evaluation that will result in regional assessment reports. These regional reports will provide a basis for part of the global effectiveness evaluation. The proposed solution also accommodates the needs associated with the evaluation process related to the global inter-regional transport assessment.

Data Users: The primary client is the COP. The vision is flexible with respect to facilitating the flow of a variety of types of data to meet a variety of possible needs, however, a special focus has been made on the data handling to allow identification of temporal trends, and to developing regionally based assessments that will feed into the global effectiveness evaluation. The establishment of a Stockholm Convention Information Warehouse will accommodate the necessary products, comprising the aggregated data arising from the regional evaluations and the global transport evaluation, and will provide transparency to the effectiveness evaluation. This warehouse would also facilitate public access to evaluation reports.

Points of consideration

A number of points were identified that will need to be elaborated further in the development of the systems to implement the effectiveness evaluation of the Stockholm Convention. These include the following:

Data ownership – data policy – recognition of data sources: While a proportion of the data generated under the POPs Global Monitoring Programme will be able to be made available for public access soon after its generation, some of the data will undoubtedly be subject to a moratorium until the scientists responsible for the data have been able to publish papers covering the results. This presents a clear constraint on the general preference for early public access to scientific data, but is one that must be allowed for in the data handling policy for raw data. Furthermore, there is a need to provide recognition of data sources, acknowledging the names of the researchers and technicians conducting the sampling and analytical procedures. Further consideration must be given to these issues by the COP or a designated subsidiary body.

In considering potential public access to data, a distinction is usually made between raw data (i.e., untreated sample measurement data) and aggregated data (i.e., data that have been subjected to forms of treatments, such as taking an average). There is often less sensitivity to publication of aggregated data as they are not as easily identifiable with specific samples or areas. These distinctions should be considered by the COP when deciding on a data policy.

The quality of the monitoring data is an important issue when determining the validity of the conclusions that can be drawn from the analysis of the data. Information on the quality of the data is often provided with the results of data analysis so that the user will have a clearer view of their validity. The proposal allows the reporting of relevant quality assurance data and information to provide the possibility of checking the quality of submitted data before including them in regional databases or using them in evaluations.

Minimum data reporting requirements need to be established to ensure consistency among the data sets between regions. These data reporting requirements should include the following: analytical measurement, with the reporting basis (e.g., dry weight); site identification and site description; sample identification; sample characteristics; sampling method; analytical method; QA/QC assessment or relevant data; data ownership. Further details of the reporting requirements will need to be determined when the monitoring programme has been specified in greater detail.

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 programme and the associated assessment methodology.

Rationale for the proposed solution

The choice of primary data storage at the regional level is consistent with the provisions of the implementation of Article 16 at the regional level to provide for regional assessments of monitoring data that will feed into the global effectiveness evaluation. Data reporting is one of the critical steps in the process and this is easier to arrange through a regional than a global network, providing for greater ease of storage, validation, and assessment of the data.

Data are expected to originate from a variety of sources, so there is a need to have a flexible solution to data management issues. In addition, a data policy will need to be developed to ensure that data from all sources meet the criteria for inclusion in the POPs Global Monitoring Programme.

Recognition must be given to the diversity in regional capabilities. This should include recognition that in some regions relevant programmes and associated data handling solutions already are in place. Clear consideration must be given to how to utilize these existing activities so as to avoid duplication and take advantage of existing expertise. This solution takes account of the fact that, in some regions at least, there already are programmes and activities for managing relevant data, some of which will comprise the POPs Global Monitoring Programme data. Not only is there a desire to make use of existing solutions, but also to avoid establishing new systems

that might inadvertently have negative consequences for existing functioning arrangements.

The proposed solution would allow for the identification of both site-specific and country-specific data within the regional assessment process, if this were desired. Nonetheless, in some regions little or no such capacity exists, so there will be a need to institute new solutions – with resource and time implications. These could initially rely on regions with capability, but the preferred option would be to develop some capacity within all regions.

It is noted that the Stockholm Convention Information Warehouse and the regional data centres that may be developed may facilitate or aid Parties meeting their obligations under Article 11 of the Convention.

Capacity Building

Until the regions have been specified, it is not possible to evaluate the extent to which data centres capable of supporting the programme exist within any given region. It is, however, likely that some regions will possess little, if any, appropriate data handling capacity. The proposed solution recommends the establishment of at least a minimal data handling capability in all regions. Consideration also needs to be given to the data handling capacity within those Parties providing raw data. In practice, this will depend on the availability of resources for capacity building. Time will also be required to establish such capacity. In the short-term, possibilities exist for technical assistance between regions to meet the existing requirements and begin the process of capacity building. In addition to the creation of new regional data handling facilities where needed, individual laboratories may need to obtain assistance to ensure the appropriate handling of monitoring data within the laboratory and its transfer to a regional data center.

Conclusions and Recommendations

1. The data communication/data management function addressed as part of this global monitoring programme is designed, as its primary purpose, to support the Effectiveness Evaluation (Article 16) of the Stockholm Convention for the Conference of the Parties.
2. The primary storage for information gathered for the effectiveness evaluation should be at the regional level. This approach will provide the flexibility required to incorporate new and existing data, provide the option for data confidentiality, accommodate existing regional database structures, build a sense of ownership within the region, and offer opportunities for capacity building.
3. Where available, existing data centres can be used for handling data at the regional level, as long as the structure and data handling practices can accommodate the minimum data requirements and the data management policy of the POPs Global Monitoring Programme.
4. Where regions do not have existing databases available, these regions should be assisted in developing a regional database suitable to support the management of the POPs Global Monitoring Programme data. This will provide an opportunity for capacity building in these regions.

5. A *data policy* needs to be developed that should, as a minimum, include the following:
   a. The process by which data, from whatever source, are submitted to a regional data centre.
   b. The data policy needs to be elaborated to recognize the concept of Data Ownership and to address public accessibility to results of monitoring activities.
6. The Conference of the Parties should establish a mechanism to oversee work with respect to the POPs Global Monitoring Programme, with responsibility for:
   a. Development and management of the Stockholm Convention Information Warehouse.
   b. Ensuring the capacity required to establish and manage regional data centers that would support preparation of the regional assessment reports.
   c. Developing the detailed data policy.
7. Guidelines should be prepared to ensure consistency of data analyses (e.g., use of standardized statistical methods) between the regional assessments.
8. In order to enhance the credibility of the effectiveness evaluation, it is recommended that all aggregated data used in the regional reports and the global transport report should be made publicly available. This will assure complete transparency of the process.

Other Issues for the Future

The following issues require further work:
- Development of detailed data/metadata requirements for regional data centres;
- Regional capacity evaluations to determine whether and where database support will be necessary;
- Development of a detailed data management policy;
- Detailed design of the Stockholm Convention Information Warehouse.

Annex 1: Definitions

1. **Data Communication**: For the purposes of this workshop, the term Data Communication encompasses the development of a well-organized collection of data containing the results of global monitoring for POPs which can be used/shared/communicated for the planned effectiveness evaluation.

2. **Data Element:** A specific piece of data with specific well defined properties for permitted values and format.

3. **Database:** A database is a collection of related information whose properties are more or less well defined. This definition does not imply any particular format for the information. A database can consist of electronic data, hard copy data, or a combination of both. In the formal electronic sense a database is a collection of data elements and their relationships to one another.

4. **Stockholm Convention Information Warehouse:** In the strictly technical sense, a data warehouse implies a specific set of design criteria, however for the purposes of this report, we are using it in a more generic sense. The Stockholm Convention Information Warehouse is a collection of aggregated data used to support the regional assessment reports, and the regional and global reports in electronic format and any other information that the COP wishes to disseminate. The purpose of this warehouse is transparency of process.

5. **Raw data:** The results of individual sample measurements or observations and related attribute data.

6. **Aggregated data:** Statistically summarized data, such as averages of a number of observations.

7. **Metadata:** Metadata are 'data about data.' These data define or describe a specific data element. Metadata generally includes ownership, spatial descriptors, data quality parameters, special conditions, data use restrictions/instructions/ cautions, etc. The types of data that are included as metadata, as opposed to a basic part of the data themselves, change with the nature of the data.

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5. PRESENTATIONS

Background and Needs for a Global Monitoring Network *by Dr. Bo Wahlstrom*

Background

- Lack of data on chemicals levels in the environment
- Adequate monitoring limited to OECD countries, Arctic, Baltic, North Sea, Great Lakes
- Analysis, evaluation and assessment of threats from individual chemicals difficult without sufficient data
- Monitoring needed for effectiveness evaluation of measures taken

3

Background: The "UNEP 12"

- Aldrin, Dieldrin, Endrin
- DDT, Heptachlor, Chlordane
- Mirex, Toxaphene
- Hexachlorobenzene (HCB)
- PCBs
- Chlorinated dioxins and furans

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Stockholm Convention

- UNEP GC Decision 18/32 (May 1995) to assess need for global instrument
- UNEP GC Decision 19/13C (Feb. 1997) to initiate negotiations
- Adopted and signed at Diplomatic Conference in Stockholm, May 2001
- Entry into force 2004
- Effectiveness evaluation +4years; 2008

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Relevant Provisions of SC

- – Control provisions:
  - Intentionally Produced POPs
  - Unintentionally Produced POPs
- – Procedure for adding new POPs

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Intentionally Produced POPs

- **Goal of the Convention:**
  - elimination of production and use of all intentionally produced POPs (*i.e.,* industrial chemicals and pesticides)
- To achieve this goal, the production and use of an intentionally produced POP will be either eliminated or restricted and, in each case, trade will be restricted
- Annex A lists 9 chemicals slated for "elimination"
  - aldrin, chlordane, dieldrin, endrin, heptachlor
  - hexachlorobenzene (HCB), mirex
  - polychlorinated biphenyls (PCBs), toxaphene
- Annex B lists 1 chemical (DDT) slated for "restriction", for which there is a specified "Acceptable Purpose"

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Unintentionally Produced POPs

- **Goal of the Convention:**
  - continuing minimization and, where feasible, ultimate elimination of the total releases of chemicals in Annex C (dioxins, furans, HCB, PCBs) derived from anthropogenic sources
- **Parties must** develop action plans within 2 years of entry into force, and implement their plans to identify, characterize and address release of chemicals in Annex C. The action plan shall include the following:
  - *evaluate current and projected releases, including development and maintenance of source inventories and release estimates*
  - evaluate efficacy of Party's laws and policies to manage such releases
  - develop strategies to reduce releases
  - promote education and training on strategies
  - review success of strategies every 5 years and report to COP
  - develop a schedule for implementation of action plan

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Identifying New POPs

- New POPs will be added to the Convention through application of scientific criteria and an agreed process for evaluation of proposed candidates
- POPs Review Committee will advise the COP on proposals submitted by Parties that must address criteria (Annex D):
  - chemical identity (names, structure)
  - persistence
  - bio-accumulation
  - potential for long range transport
  - adverse effects
- Party must also include a statement of reasons for concern and need for global control

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Identifying New POPs

- **POPs Identification Criteria:**
- **Persistence:**
  - evidence that the half life of the chemical is > 2 months in water, or > 6 months in soil or sediment, <u>or</u>
  - evidence that the chemical is sufficiently persistent to warrant consideration under the Convention
- **Bio-accumulation:**
  - evidence that bioconcentration factor or bioaccumulation factor in aquatic species is > 5000, or absent such data, that log K_{OW} > 5, <u>or</u>
  - evidence that chemical presents other reasons for concern (*e.g.,* high bioaccumulation in other species, high toxicity or ecotoxicity), <u>or</u>
  - *monitoring data in biota* indicating that bioaccumulation potential of chemical is sufficient to warrant consideration under Convention

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Identifying New POPs

- **POPs Identification Criteria (continued):**
- **Potential for long range transport:**
  - *measured levels of chemical in locations distant from sources of release* that are of potential concern, <u>or</u>
  - *monitoring data showing that long range environmental transport of chemical may have occurred*, <u>or</u>
  - environmental fate properties and/or model results show that chemical has potential for long-range environmental transport: if chemical migrates significantly through air, its half life in air should be > 2 days
- **Adverse effects:**
  - evidence of adverse effects to human health or environment that justifies consideration under Convention, <u>or</u>
  - toxicity or ecotoxicity data indicating potential for damage to human health or environment

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Identifying New POPs

- **Information for Risk Profile (Annex E):**
  - sources (production data, uses, releases, etc.)
  - hazard assessment for endpoint(s) of concern
  - environmental fate (chemical and physical properties, persistence, environmental transport, degradation and transformation, etc.)
  - bioconcentration or bioaccumulation factor
  - *monitoring data*
  - exposure and bioavailability data
  - national and international risk evaluations, assessments, etc.
  - hazard classification and labeling information
  - status of the chemical under international conventions

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Research

- **Research, development, monitoring and cooperation:**
- Parties shall, within their capabilities, encourage and/or undertake these actions on all aspects of POPs and their alternatives, including on:
  - environmental releases
  - *trends in levels in the environment and humans*
  - transport, fate and transformation
  - effects on humans and the environment
  - socio-economic impacts
  - release reduction and/or elimination

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Reporting

Parties shall report to the COP on:
- measures taken by Party to implement the Convention
- effectiveness of the measures taken

Parties shall provide the Secretariat:
- data on, or estimates of, total quantities of POPs in Annexes A and B that were produced, imported and exported
- list of States from which it has imported or to which it has exported POPs in Annexes A and B

COP will specify frequency and format of such reports

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Effectiveness evaluation

- **Effectiveness Evaluation:**
- COP must evaluate effectiveness of Convention in reducing and/or eliminating releases of POPs:
  - *this will be done by establishing a mechanism to acquire comparable monitoring data on:*
    - *presence, levels and trends of POPs in environmental and biological media, and*
    - *regional and global environmental transport of POPs*
  - *mechanism will tap into existing national, regional and global networks and sources of information*
  - as COP must review first effectiveness report 4 years after Convention enters into force, COP1 must address this issue

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Effectiveness Evaluation (Article 16)

- Secretariat to prepare report (for INC7) on its efforts to:
  - address needs for environmental monitoring and evaluation to evaluate effectiveness of the Convention
  - develop guidance on evaluation of effectiveness
  - identify basic data needs and data gaps
  - assess the capacity of existing effectiveness evaluation programs under other MEAs
  - initiate arrangements for providing comparable monitoring data, including facilitating arrangements where information is not available
  - compile guidance for the collection of relevant data

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Implementation Aspects

- Convention will enter into force 90 days after 50th ratification
- COP will be established to oversee implementation:
  - must meet within 1 year of entry into force
    - thereafter at regular intervals
  - must review effectiveness of convention commencing four years after entry into force, and periodically thereafter:
    - COP1 will arrange for:
      - comparable monitoring data on presence of POPs and regional/global environmental transport, and
      - reports on monitoring, on regional and global basis
  - COP1 to establish POPs Review Committee
- UNEP will provide secretariat

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Convention Status

- During the signature period (23 May 2001-22 May 2002):
  - 150 countries + EU signed the Convention
- Ratification, acceptance or accession decisions:
  - 30 Parties (to date)
- INC-7 will be held July 14-18, 2003 (Geneva)
  - preparations for COP1
  - implement Stockholm resolutions
  - priority focus on NIPs & financial & technical assistance
- Convention text & information are on UNEP POPs home page:

www.pops.int

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**GEF: Regionally Based Assessment
of Persistent Toxic Substances**

- Project period September 2000 to April 2003
- Data collection phase finished
- Technical Workshops on sources, levels, effects finalized
- Regional Priority Setting Meetings held to discuss the draft Regional Report, June to October 2002
- Task force to prepare review paper on alternatives to PTS
- Global Priority Setting Meeting to discuss draft Global Report mid-March 2003
- Global Report highlighting major issues mid-2003

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Workshop Objectives *by Ms. Francesca Cenni*

Workshop to Develop a POPs Global Monitoring Programme to Support the Effectiveness Evaluation of the Stockholm Convention on POPs

Objective:

**Develop guidance for a POPs
Global Monitoring Programme
for consideration by the POPs
INC7 in June 2003**

GLOBAL POPs MONITORING WORKSHOP

The workshop will present a framework for the establishment of

"Arrangements to provide *the COP* with comparable monitoring data "

required for effectiveness evaluation of the Convention

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GLOBAL POPs MONITORING WORKSHOP

The workshop will be divided into different working groups addressing key items for the development of a monitoring programme:

Each working group will develop and propose solutions for one of the key monitoring issues

GLOBAL POPs MONITORING WORKSHOP

The working groups will concentrate on:

1) **Assessment needs for the Stockholm Convention**

2) **Substances and analytical techniques**

3) **Sample Matrices, Site Selection and Sampling Techniques**

4) **QA/QC and Data Treatment**

5) **Data Communication**

GLOBAL POPs MONITORING WORKSHOP

Capacity Building should be considered by each working group having to describe the capacity necessary to implement the monitoring aspect discussed in the working group

GLOBAL POPs MONITORING WORKSHOP: Objectives

ASSESSMENT NEEDS FOR THE STOCKOLM CONVENTION:

- Describe different strategies to execute the effectiveness evaluation of the Stockholm Convention

- Describe the minimum monitoring information needed for the evaluation

- Describe how to assess long-range transport

GLOBAL POPs MONITORING
WORKSHOP: Objectives

SUBSTANCES AND ANALYTICAL
TECHNIQUES

- Discuss the possibilities for setting priorities between the twelve POPs in different parts of the world
- Overview of analytical techniques required to produce data for trend determination
- Describe a strategy for the programme to use a tiered system of laboratories

GLOBAL POPs MONITORING
WORKSHOP: Objectives

SAMPLE MATRICES, SITE SELECTION
AND SAMPLING TECHNIQUES

- Give recommendations on site selection and matrix selection (substance specific)
- Define how matrices can be selected for regional or global assessments
- Recommend a sampling strategy (resolution, frequency etc.)

GLOBAL POPs MONITORING WORKSHOP: Objectives

QA/QC AND DATA TREATMENT

- Make recommendations on the use of reference materials
- Define the requirements of QA/QC procedures
- Set a strategy for Intercalibration exercises
- Metadata needs for QA/QC evaluation

GLOBAL POPs MONITORING WORKSHOP: Objectives

DATA COMMUNICATION

- Define a communication strategy for the global programme
- Describe how data can be published in Internet, addressing confidentiality, and data dissemination
- Propose strategies and approaches for building a data warehouse
- Draft a policy for data handling
- Discuss the opportunity to build geographic information systems

Assessment Needs for the Stockholm Convention *by Dr. David Stone*

ASSESSMENT NEEDS FOR THE STOCKHOLM CONVENTION

David Stone (Canada)

Article 16

- Requires that the Conference of the Parties (COP) shall periodically evaluate the effectiveness of the Convention
- Evaluation to Include:
  - National reports
  - Non-compliance information
  - **Assessment of Environmental Monitoring Data.**

Impetus

- Evaluation 4 years after entry into force
- To do this the Conference of the Parties (COP) must:
  - establish monitoring capacity where it does not already exist (~2yrs)
  - organize an assessment of the resultant information (~2yrs)
  - develop an evaluation framework (the task at hand)

Strategy review

- Elements of review
  - boundaries of the task;
  - lessons from other monitoring programmes;
  - fundamental criteria for global monitoring;
  - organizational options;
  - minimum information needs;
  - the role of modeling;
  - modalities for capacity building; and,
  - a possible operational framework to move data through to assessment.;

1) Analysis of the boundaries

■   Boundary observations

1. Evaluation is not concerned with National Reports or with non-compliance, and it is not intended as a tool to detect "hot spots"
2. Implementation by parties through participating in a regional programme
3. Obligatory only to consider substances contained in the Annexes. Thet need not all be measured in all components of the sampling matrix; and,
4. Prime purpose is to detect temporal trends (essential for effectiveness evaluation)

■   Boundary observations (cont'd)

5. Not required to contribute to the science of POPs or dossiers for new substances
6. Opportunities for strategic regional capacity building
7. Identify the minimum data set necessary to inform the COP on trends
8. Non-parties are encouraged to contribute acceptable information if they wish. However, countries participating in this way would be "passive" contributors

Lessons learned from other programmes

- Inclusiveness and transparency
- The objective of the task must be repeatedly emphasized and understood.
- The value of clarity of: design; of expectations; and of arrangements for QA/QC.
- Simplicity is beautiful.
- Arrangements must be sustainable.
- The value of plasticity.

Lessons learned (cont'd)

- A tiered approach to preserve simplicity while allowing the programme to vary intensity of effort.
- Clear understanding of data ownership.
- Unencumbered access to data for the assessment
- Use of "thematic data centres" for mediation of QA/QC and data availability
- Clear accountabilities for those involved in the assessment

Fundamental criteria

- The boundary observations from Section 1 and the "lessons learned" from Section 2 provide a list of criteria which may assist decision-making during the design and implementation of the programme.

4. Organizational options

- I. National
  - Every Party responsible for collecting and analyzing data according to global standard
  - National assessment of data or assessment by international team
  - Hierarchy of reports – national, regional and global

I. National

- Advantages
  - inclusive
- Disadvantages
  - lack of analytical capacity
  - unsustainable to build capacity with this program alone
  - QA/QC requirements very difficult to meet
  - lack of data comparability
  - not indicated in Article 16 and is not compatible with the use of existing programmes and mechanisms

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- II. Global organization

  - Global coordination unit
  - Collection of data by invited parties and international organizations by standardized methods
  - Use of limited number of accredited laboratories not necessarily in same region of samples origin
  - Global team conducts assessments in both regional and global formats

II. Global organization

- Advantages
  - global harmonization
  - potential for global assessment of temporal trends and assessment of regional and global transport
  - cost effective
- Disadvantages
  - difficulty ensuring global data comparability
  - limited potential for capacity building
  - exclusive – distances parties from the process
  - inflexible with respect to regional differences
  - Does not accommodate potential desired regional focus of parties

- III. Regional organization

  - Regional coordinating and assessment nodes under global coordination unit
  - Sampling at the national level, analysis and interpretation at the regional level
  - Regionally produced assessments on temporal trends
  - Global reporting to summarize regional reports
  - Potential for some assessment of interregional transport
  - Requires division of globe into regions

III. Regional organization

- Advantages
  - encourages ownership among Parties
  - balance between practicality and inclusiveness
  - flexibility for regional differences in the environment and capacity
  - A managable number of participating laboratories with harmonized methodology and QA/QC would allow for evaluation of trends and regional transport
  - cost effective
  - shared regional capacity

III. Regional organization

- Disadvantages
  - Regionalization of data collection would complicate comparisons between regions and assessment of inter-regional transport
  - Must balance between firm global guidance (to achieve goals of effectiveness evaluation) and keep responsibility at the regional level
  - Assistance for some regions needed

Suggestions for Minimum Information Needs (driven by SIMPLICITY to give SUSTAINABILITY

- Small number of sample types focused on evaluating Convention effectiveness
- All substances need not be monitored at all locations – optimize plan
- Global comparability is not practical therefore assessments should be conducted at a regional level

Suggestions for Minimum Information Needs

- Regional sample representation is not possible – ensure samples are representative of the site
- Establish agreed upon rationale for site selection –not within influence of local sources
- Air monitoring stations can provide information on trends and regional/global transport Ethical, cultural and religious issues of sampling human material – use of existing programmes

UNEP Workshop to Develop a Global POPs Monitoring Programme to Support the Effectiveness Evaluation of the Stockholm Convention

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Conclusion

- The objectives of article 16 can be achieved with a modest sampling matrix and modest number of samples.

A possible operational framework

- The optimum approach is likely to be built around a series of regional assessments (Option 3).

a. develop framework overseen by a global advisory/steering group

   - Scientists and bureaucrats from the Parties and international, industry and NGO organizations that would contribute work.
   - produce strategic guidance document establishing:

     - An agreed division of the globe into regions:
     - A fundamental sample/media matrix;
     - Agreed sampling and analytical methodologies;
     - Protocols for QA/QC;
     - Protocols for compilation of regional assessments;
     - A tiered capacity approach; and,
     - Include a draft annotated generic table of contents for each regional assessment.

b. The convention secretariat would provide (or make arrangements for) coordination / management services to the global advisory group, including maintaining the website already launched by UNEP Chemicals.

c. regional advisory groups responsible for:
- Transforming the global sampling and media matrix into a regional reality.
- Deciding on the number of participating laboratories within each region.
- Regionally implementing the globally agreed measures for QA/QC.
- Working with the Convention Secretariat to help develop a tiered approach for laboratory infrastructure
- Work with National focal points
- Establishing a regional assessment group

d. National focal points

e. Expert group to identify several optional practical products for evaluating "regional and global transport" and indicate the required tools for each option at both a regional and global level.
- global advisory group to review

f. global assessment group to consolidate regional reports into a global statement.

Final comment

- Article 16 is an innovative feature of the Stockholm Convention.
- It is essential to ensuring that the Convention is a living agreement that can evolve intelligently over time.
- It will be a challenging task.
- To succeed always seek simplicity at every stage.

Substances and Analytical Techniques *by Dr. Derek Muir and Dr. Masatoshi Morita*

Substances and Analytical Techniques

Derek Muir[1] and Masatoshi Morita[2]

[1]National Water Research Institute, Burlington, Ontario, Canada
[2]National Institute for Environmental Studies, Tsukuba, Ibaraki, Japan

Objectives

1. **Describe how to set priorities for the substances in different regions**
2. **Recommend analytical techniques to be used in order to develop comparable data on environmental levels globally**
3. **Define the capacity necessary for implementation of our recommendations**

Priorities for substances

Actual analytes

- **aldrin, dieldrin, endrin** …………………... **…3**
- **chlordane, heptachlor** …………………... **…7**
- **toxaphene** ……………………………….. **…3-25**
- **mirex** ………………………………………… **…2**
- **dichlorodiphenyltrichloroethane (DDT)...** **…6**
- **hexachlorobenzene (HCB)** ……………... **…1**
- **polychlorinated biphenyls (PCBs)** …….. **…7- ~180**
- **polychlorinated dibenzo-*p*-dioxins and – dibenzofurans (PCDD/Fs)**…….....……… **…17**
- **non-ortho/mono-ortho substituted PCBs with TEFs** …………………………………... **…11**

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Complex substances

- **chlordane** - includes heptachlor, octachlor, & nonachlor isomers, plus metabolites heptachlor epoxide and oxychlordane usually all quantified by use of individual standards
- **toxaphene** – often quantified using the technical mixture or using individual chlorobornanes e.g. P26, P50, P62
- **mirex** – could include photomirex
- **DDT** – o,p'- and p,p'-substituted isomers of DDD, DDE and DDT but others might be of interest, e.g. DDA, DDMU
- **PCBs** – "ICES" 7 (28/31, 52, 101, 118, 138, 153, 180)
  - "AMAP 30"; lists from other programs
- **PCDD/Fs** – non-2,3,78-substituted congeners may be of interest re sources but are not routinely determined

Matrices to be analysed will influence substance priorities

- **Abiotic samples** (air, water, snow, passive samplers, soil and sediments) –
  - transformation products less important
  - more components of technical products are present e.g. PCB and toxaphene congeners
  - more co-elution problems e.g. PCB153/132/105
  - non-2,3,7,8-substituted PCDD/Fs are important
- **Biological samples** (plants and animal tissues) –
  - fewer components detectable especially in homeotherms
  - metabolites more important, e.g. oxychlordane, p,p'-DDE
  - technical mixtures do not quantify POPs well, e.g. toxaphene
  - non-2,3,7,8-substituted congeners not important

Priorities for substances in different Regions. Should they be the same everywhere?

Pros

- some POPs *may* have had little or no use in a given region e.g. toxaphene, mirex
- some POPs may be difficult to analyse with prevailing methodology and analytical capacity in some regions
  - aldrin/dieldrin/endrin in biota – degraded during acid cleanup step
- Regional interests might be more on biota than on abiotic samples
- Regional capacity may be limited or non-existent
  - PCDD/Fs and *no*-PCBs due to requirement for GC-HRMS

Cons

- Completely omitting substances defeats the purpose of a global assessment required by Article 16

Priorities for substances - *continued*

- Decision to omit some POPs or not depends on how "regions" are defined, how the program is financed and ultimately on structure of the monitoring program
- Numerous labs are capable of basic OC pesticide and PCB congener analysis so little reason to omit them
- Relatively few, if any, labs in Africa, south Asia and South America are determining toxaphene, PCDD/Fs and *no*-PCBs.

- one option is to categorize the chemicals as Essential, Essential-sub-regional (ES) or Recommended. The ES category would allow some countries or regions to opt out either because the analyte was not of interest or because of analytical concerns.
- another option is to take a Tiered approach to monitoring so that some regions with full capability do "non routine" analyses on samples or extracts from other regions

Tentative Conclusions/recommendations re priorities for substances

- A list of individual PCB congeners (at least 30) and OCPs and metabolites (at least 20) should be selected.
  - At a minimum the "ICES 7" PCBs should be used.

- consideration should be given to applying a regionally based rating system like that of AMAP's for individual compounds

- Toxaphene and PCDD/Fs should be included but may have to be in the "recommended" rather than "essential category" due to analytical considerations

Analytical techniques

Considerations here include:
- will the global monitoring strategy include developing new laboratories, and/or training programs for lab personnel, in certain regions which have relatively few facilities and experience?
- will the strategy include a tiered series of existing labs with increasing degree of capability for all analytes?

- assumption: that well equipped labs headed by analytical chemists with some experience in analysis of POPs will be selected for the program on a regional basis.
  - These labs and individuals will already have analytical methods running for some matrices but may need guidance for others.

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Analytical techniques - the basics

1) **Sample preparation**
2) **Extraction**
3) **Clean-up using partition & chromatographic fractionation**
4) **Separation by gas chromatography (GC)**
5) **Detection with selective and sensitive detectors.**

Extraction & isolation of PCBs and OC Pesticides (OCPs)

• Numerous methods have been published over the past 30 years for determination of PCBs and OCPs in food and environmental matrices

• Laboratory standard operating procedures for analysis of PCBs & OCPs are available from:
   • **US EPA and NOAA (Status and Trends Program)**
   • **ICES (Techniques in Marine Environmental Sciences)**
   • **OSPAR (Joint Assessment and Monitoring Program)**
   • **International organization for Standardization (ISO)**
   • **Association of Official Analytical Chemists International**
   • **Japan Environment Agency**
   • **Gosstandard of the Russian Federation**

• In most cases these SOPs also include detailed sample preparation steps

• They usually do not include recommendations for archiving of samples or sample extracts

Gas chromatographic detection systems for POPs analysis		
GC detector	**Analytes**	**Advantages/disadvantages**
Capillary GC – with ECD	All o-PCBs & all OCPs except toxaphene	Relatively inexpensive and easy to operate. Similar response factors for most Ocs; Good sensitivity. Adequate for routine tasks. High potential for mis-identification of some POPs due to co-eluting peaks
GC-Quadrupole MS in EI mode	All PCBs & all OCPs except toxaphene	Moderately expensive and more complex to operate and maintain. Newer instruments (post 1997) have adequate sensitivity for routine POP at low pg/uL Much less potential for mis-identification than with ECD
GC-Quadrupole MS in ECNI mode	Toxaphene and other OCPs	Comparable sensitivity to ECD in SIM mode for some POPs, in ECNI mode. Much less potential for mis-identification than with ECD
Ion trap MS in MS/MS mode	All PCBs, All OCPs	Comparable sensitivity to ECD in MS/MS mode for some POPs. Much less potential for mis-identification than with ECD
High resolution MS in EI mode	PCDD/Fs, all PCB/OCPs except toxa	Comparable sensitivity to ECD in SIM mode. Highly reliable identification at low pg/uL levels.

Special considerations for abiotic samples

- water, passive samplers, soils and sediments, especially from remote locations, can be inadvertantly contaminated during sampling (e.g. by OCPs, PCBs or PCDD/Fs)
- Less of a problem for biota where subsamples are prepared in the laboratory
- laboratory air can be contaminated by PCBs from building materials and possibly by OCPs used for insect control
- Guidelines will be needed to help assure that labs are free of significant contamination.
- Ideally this would involve a well ventilated lab with air prefiltered through HEPA and carbon filters but any clean chemical laboratory facility should be adequate

Tentative Conclusions/recommendation

- For ortho-substituted PCBs and OCPs, no single, detailed, step by step, analytical method is recommended
- Critical to the success of this approach would be strong intralab and interlab QA guidelines
- The monitoring for ortho-PCB and OCPs can be "unified" using an interlaboratory calibration program
- Abiotic samples may require special considerations given potential for contamination on sampling and in lab preparation steps

- A useful activity for the Global POPs Monitoring program might be to prepare a list of agencies and the addresses and titles of the recommended laboratory SOPs for POPs analysis.

Determination of PCDD/Fs and no-PCBs

- Analytical methodology differs from that for other OCs:
  - much lower detection limits (typically 10-100 times lower) required because of low TDIs
- methodology for PCDD/Fs uses isotope dilution MS (^{13}C-surrogates for all PCDD/F homolog groups)
  - enrichment on carbon to isolate planar compounds
  - very small final volumes (10-50 uL) for GC analysis
  - GC-high resolution mass spectrometry for quantitation

- Methodology for PCDD/Fs, slightly modified to include no-PCBs, developed by the US EPA (1998;1999) is well established and validated by numerous interlab comparisons.
- This methodology or something similar would be recommended for use in a global monitoring program.

Consideration of Detection limits (DLs)

- presents some challenges for the global POPs program especially when multiple laboratories in different regions are involved
- instrumental DLs will be similar
- Method detection limits (MDLs) depend on the analytical method but also on the sample size and QA considerations e.g. information available from blank or control samples and recovery studies.
- for example: MDL=blank+3*SD of blank or low level standard
- selection of detection limits also depends on the goals of program
  - need to balance reliability of the results versus need to achieve broad geographic coverage and avoid reporting "less thans" for a high proportion of samples

Further Tentative Conclusions/recommendations on analytical methods

- A specific method (EPA 1613 and 8290A) for the extraction, isolation and quantification steps for PCDD/Fs (along with no-PCBs) is recommended
  - to be in compliance with ongoing programs and compatible with results generated with these methods over the past 10 years.
- The amount of guidance needed for analytical methods will depend on whether UNEP POPs monitoring strategy includes developing new laboratories, and/or training programs for lab personnel, in certain regions which have relatively few facilities.
- Close attention should be paid to detection limits in planning the monitoring program so that the amount of usable data, i.e. >MDL, is maximized.

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Sample Matrices, Site Selection and Sampling Techniques *by Prof. Kevin Jones and Mr. J.L Barber*

Sample Matrices, Site Selection And Sampling Techniques

K. C. Jones and J. L. Barber

Environmental Science Department,
Lancaster University, UK.

What are we trying to do?

- Show *source reduction*? If so, sources to what?
- Show *exposure reduction*?
  - For humans
  - For susceptible biota

- Show *effects reduction*? If so, how?

- Are there cost-effective strategies, which can provide meaningful information, without requiring elaborate, multi-country, multi-media and highly time resolved data?

Techniques must detect TEMPORAL TRENDS….

PBDEs: Anna Palm (*Pers. Comm.*) PCBs: Breivik et al (2002)
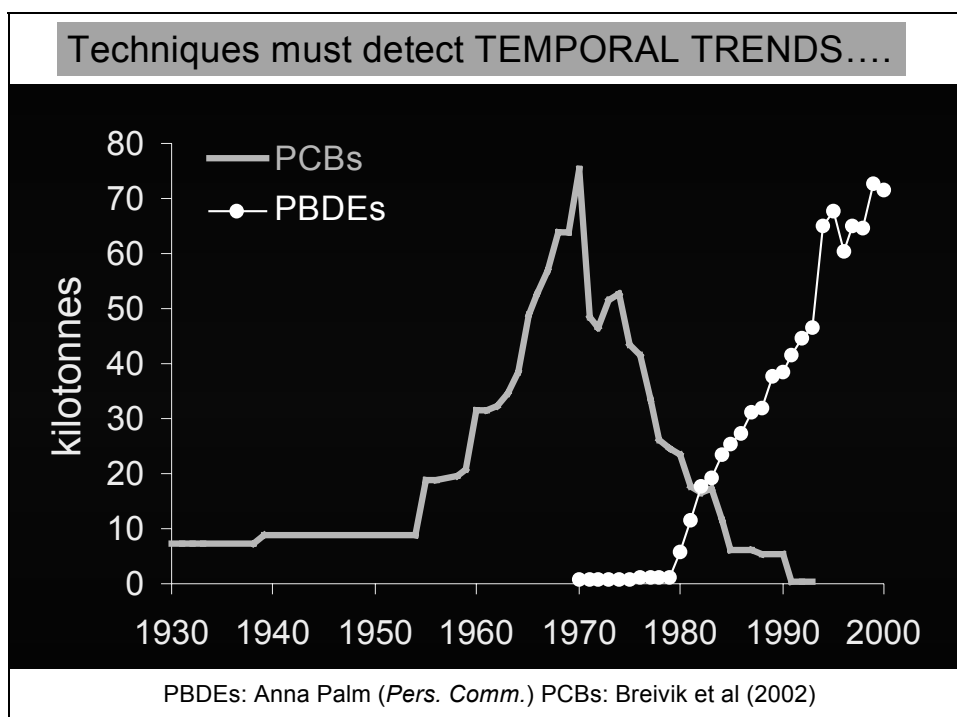
Time…..

- What timescales are envisaged (months – years – decades)?
- Different media will have different response times to a reduction in use/emission
- There is much short-term variation e.g. seasonally; 'noise' in biological data
- What are the implications for sample frequency?
- Should sampling be concurrent at different locations regionally/globally, and for different media? e.g. air in the north and south hemisphere

Techniques must detect spatial trends....to help identify sources

Global PCB Emission

< 0.1	0.1 - 1	1 - 10	10 - 50	50 - 100	100 - 500	> 500
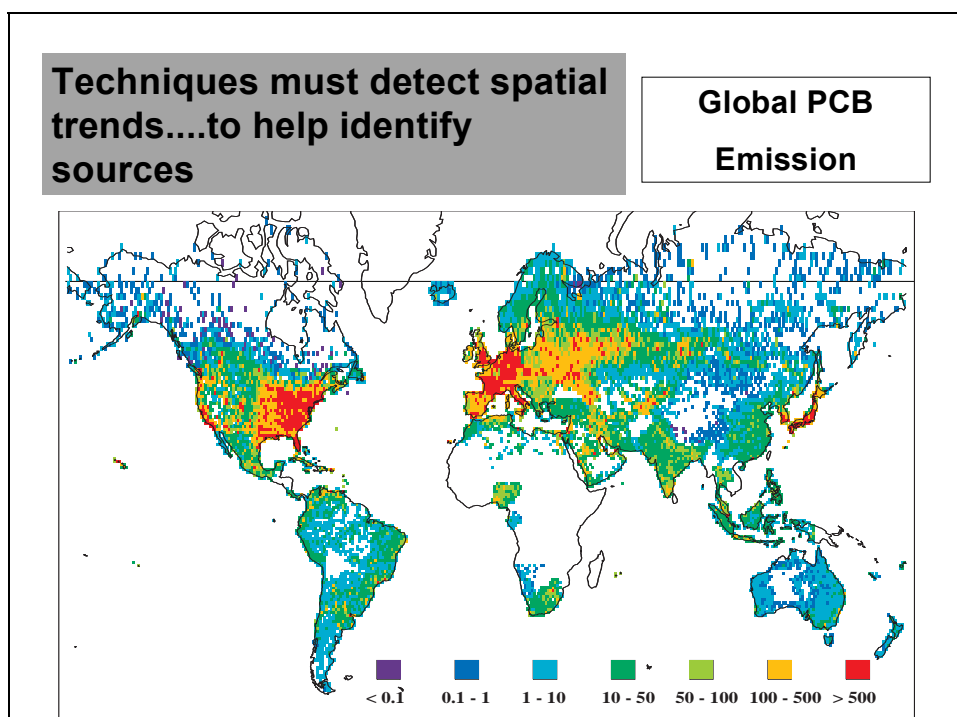
What media should be considered for monitoring purposes?

- Air?
- Water?
- Soil?
- Sediment?

- Vegetation?
- Wildlife?
- Foodstuffs?
- Human samples?

Air

- **Air a key medium -responds quickly to sources**

- **Air concentrations fluctuate widely in space and time**

- **Different phases and different concentrations - compromises over sample time/volumes**

- **Short-term sampling/bulking etc?**

- **Learn from existing national/regional programmes (e.g. IADN in Canada/US; EMEP)**

Active sampling – cost, training, power, supporting met data

Establish regional 'super stations'?

Passive sampling – low cost, high spatial resolution, easy, semi-quantitative…, still being optimised, different designs for different purposes

XAD-Resin Based Passive Air Sampling System For POP

15.5 cm
10.5 cm

stainless steel lid

carabine & loop

resin-filled stainless steel fine mesh cylinder

adjustable hose clamps

bottom part of stainless steel shelter

29.5 cm
20 cm

2 cm

coarse mesh

Wania et al. *Environ. Sci. Technol.* **2003**, ASAP.

Hexachlorocyclohexanes Across North America

α-HCH

γ-HCH
lindane

ng/sampler

ng/sampler

- ◉ relatively uniform across Canada and US
- ◉ highest levels in Atlantic Canada
- ◉ low levels in central America

- ◉ large differences across North America
- ◉ highest levels in Canada Prairies

Mapping POPs in the Great Lakes Basin

Meteorological Service of Canada (Tom Harner)
Lancaster University (Kevin Jones)
Health Canada (Jiping Zhu)

- • **PUF disk passive air samplers**

- • **~25 sites**

- • **3 month integration (started July 2002) (summer, fall, winter, spring)**

- • **equivalent ~400m³ sample volume**

- • **targets - PBDEs, PFOS precursors and OCs**

- • **indoor vs outdoor air – Ottawa, Canada (80 homes, winter 2003)**

Lake St. Clair
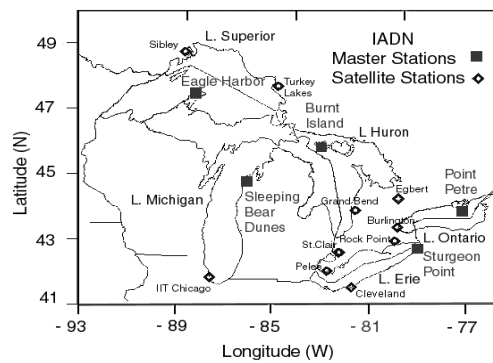
PASAE PROGRAMME – LANCASTER STUDY ACROSS EUROPE

PCBs in PUF disks – big urban – rural gradients

Highest/ lowest = 113
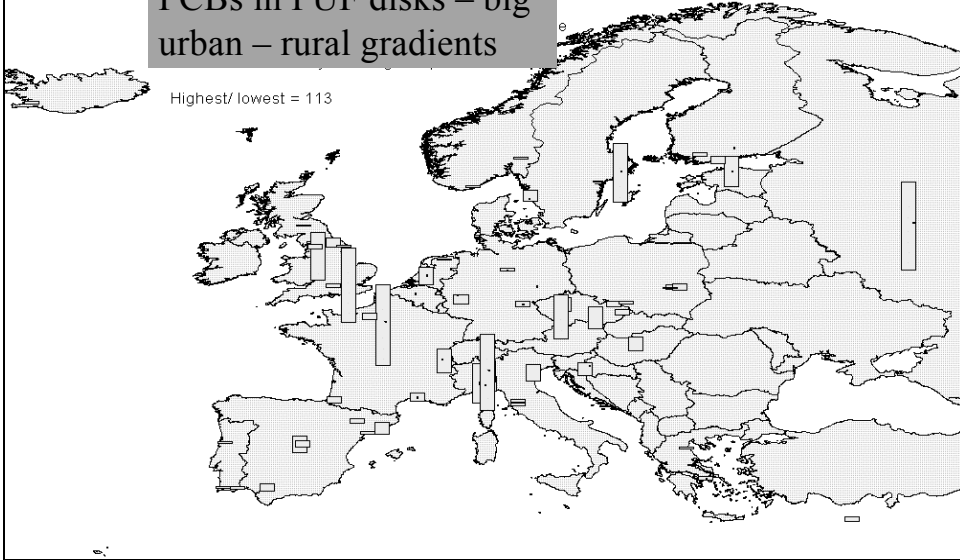
PBDEs – UK has had high usage
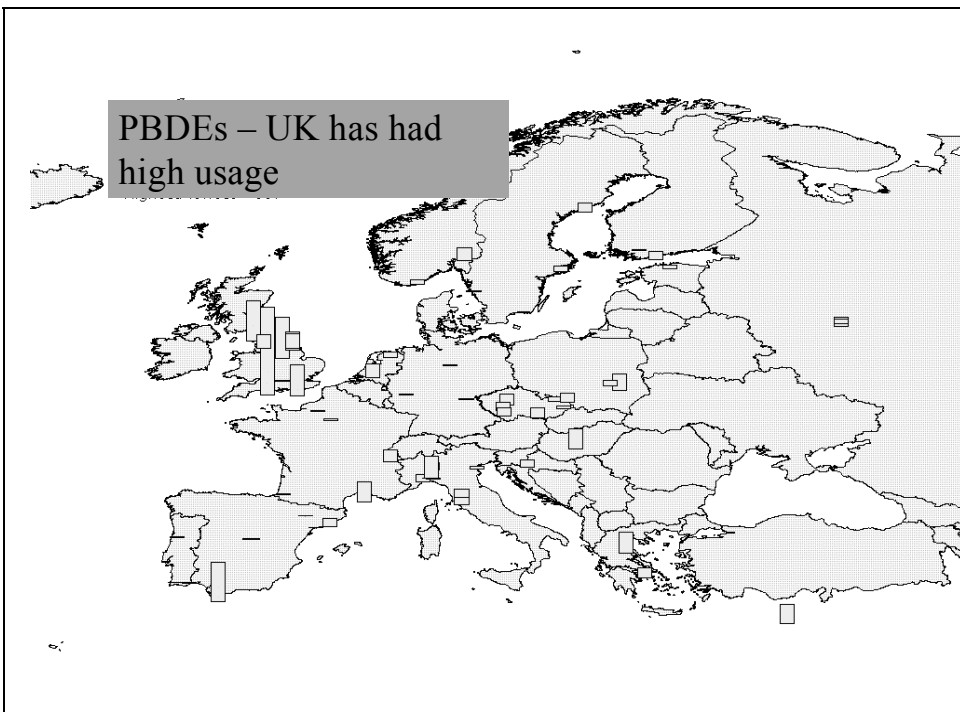
Sampling of 'water'

- Advantages of time integration and 'enrichment' of concentrations. Techniques include:

- Fish

- Passive samplers – e.g. SPMDs

- Mussels – the international 'Mussel Watch' programme for coastal waters

    Ubiquitous, convenient, easy way of conducting spatial/temporal trend studies of coastal waters.
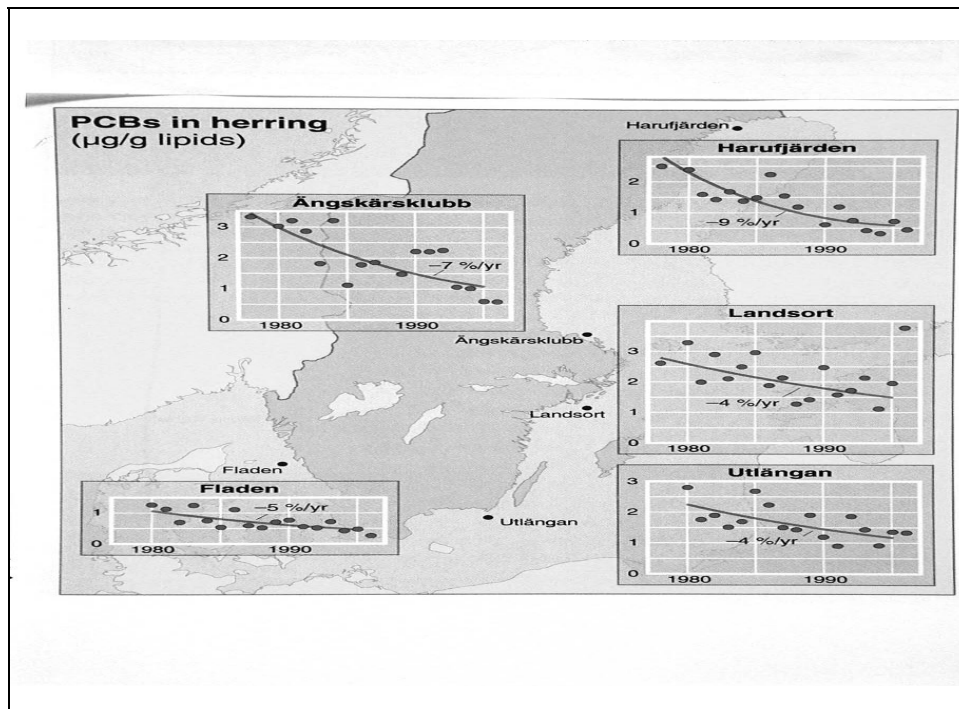
Soils and sediments

- High environmental burdens – important for global balances

- Slow response times

- Background soils and sediments reflect spatial differences in cumulative atmospheric deposition/net air-surface exchange

- Very heterogeneous - important questions of depth, ecosystem type etc.

- Can show spatial trends, but poor for time trends

Wildlife

- POPs bioaccumulate in animals because of their high lipid content and their long lifetimes

- Some POPs bioconcentrate up food chains

- Choice of species/matrix?

- Species range and ecosystem differences

- High variability in biological systems

- Birds eggs; marine mammals
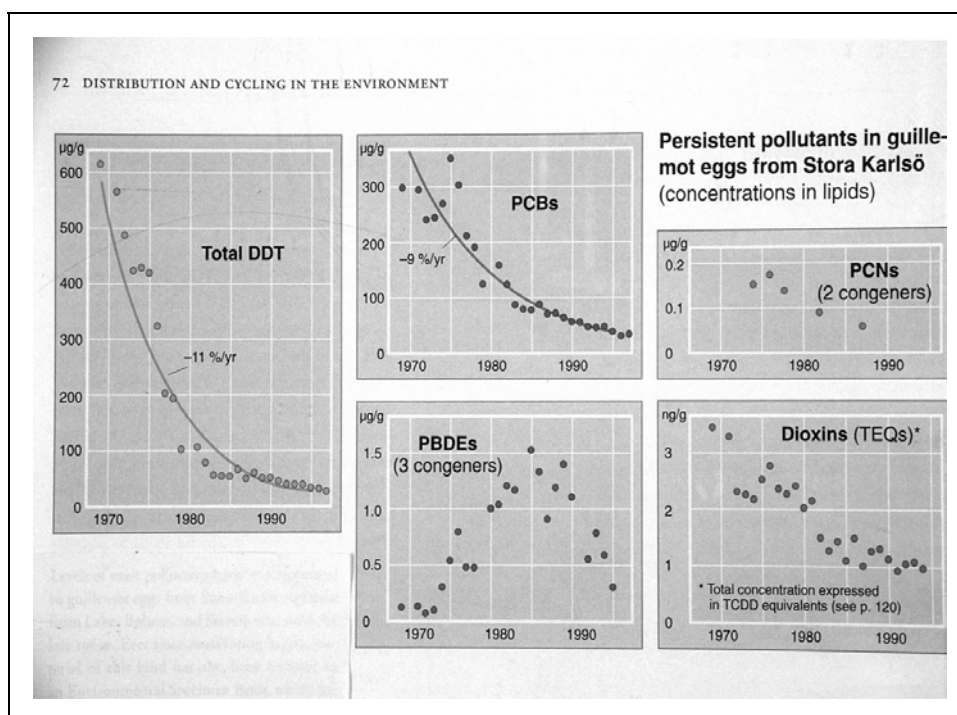
Human foodstuffs

- Link between 'environment' and 'exposure'
- Many countries already have food sampling programmes
- Agricultural animals – wide distribution & 'control' - milk, eggs

  ✓high concentrations

  ✓clear AIR – GRASS – COW – FOOD link

  ✓easily homogenised, pooled to represent a large area

  ❖BUT, also affected by husbandry practices

EU - milk monitoring, for source and exposure reduction
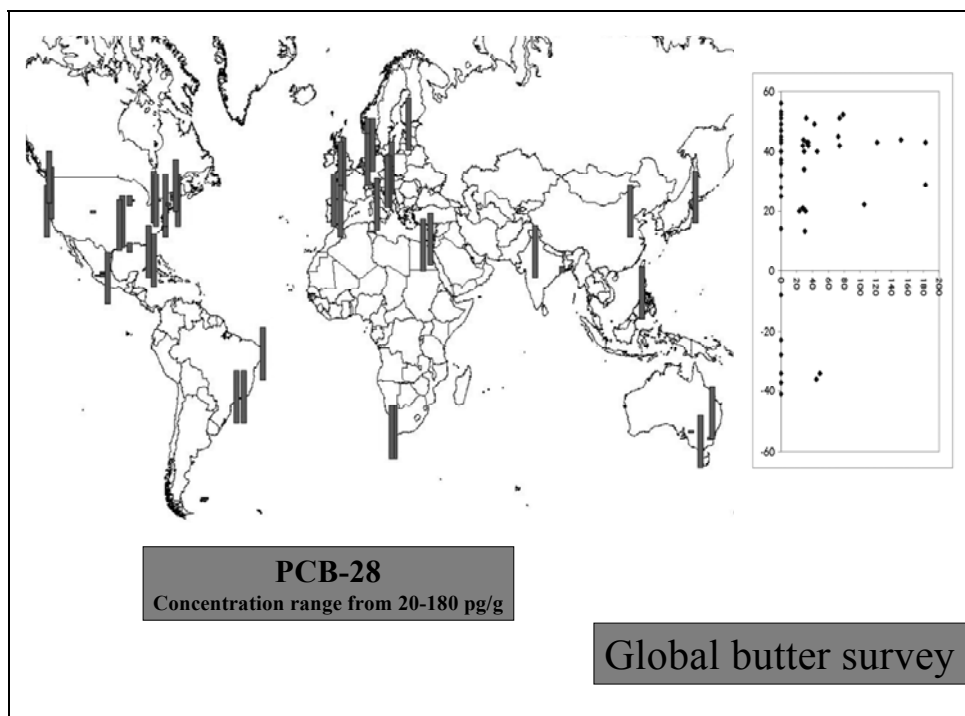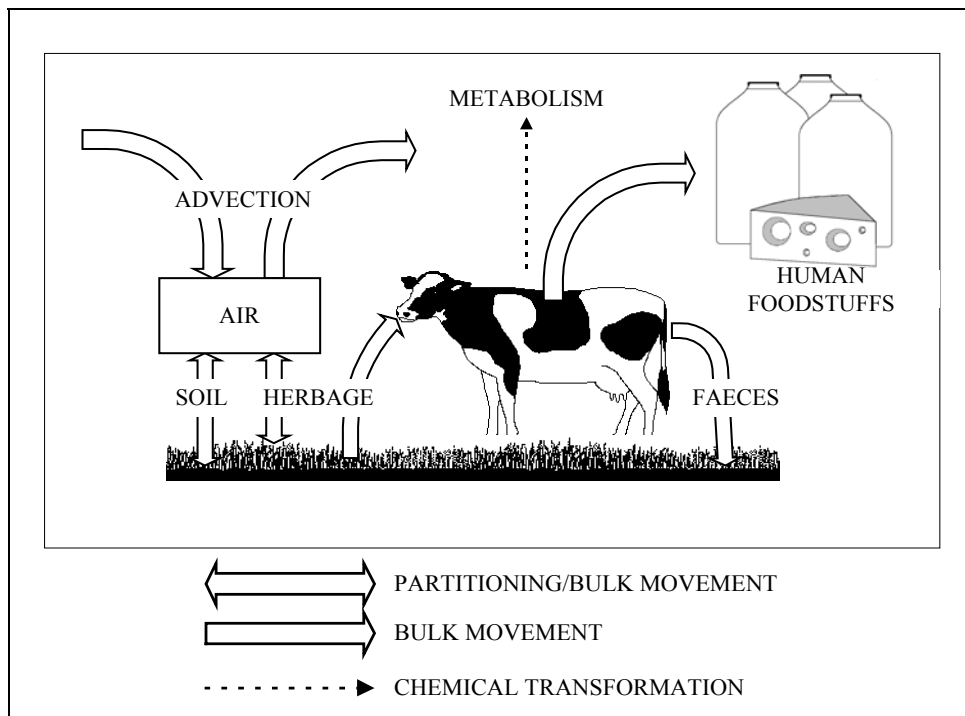
Human tissues

- Humans - truly global distribution, which allows complete spatial mapping of POPs in the global environment.

- Direct, integrated measure of exposure – is source and exposure reduction working?

- Blood – variable but easy to sample; existing programmes?

- Milk – babies are key sub-group; better integrator?

Sampling strategies

- Sampling should be designed to enable multiple analyses to be conducted
- QA/QC at the point of sampling…
- Should sampling being 'concurrent'?
- Frequency of sampling required to detect trends?
- Number of analyses required to detect trends?
- What are the advantages/disadvantages of pooling samples?

Quality Assurance/Quality Control and Data Treatment *by Dr. Jacob de Boer*

Quality Assurance/Quality Control and Data Treatment
UNEP POP Workshop, 24-27 March, Geneva

Jacob de Boer
Netherlands Institute for Fisheries Research

RIVO

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QA/QC

- Reference Materials
- Interlaboratory Studies
- Quality of Data
- Data presentation

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Reference Materials

- Laboratory Reference Materials (IRM or LRM)
- Certified Reference Materials

RIVO

WAGENINGEN UR

RIVO
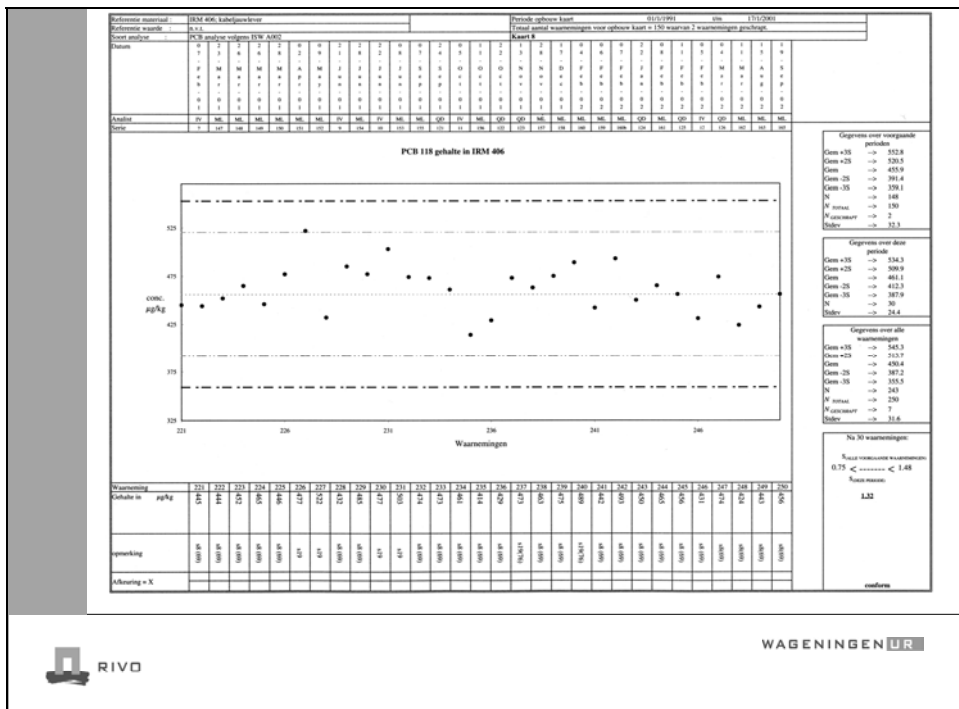
WAGENINGEN UR

CRM Quality Criteria

- Matrix: Freeze-dried/oil/wet material
- Certified or indicative values
- Spiked or non-spiked
- Realistic concentrations
- Transportation limitations

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CRMs for POPs in Biota

CRM		c-C	t-C	diel	diox/furan	DDT	HCB	mirex	PCB
SRM1974a	mussel	X	X			X			X
SRM1588a	cod liver	X		X		X	X		X
SRM1945	whale bl.	X				X	X	X	X
SRM2974	mussel	X	X			X			X
SRM2977	mussel	X		X		X			X
SRM2978	mussel	X	X	X		X			X
140/OC	plant			X		X			X
BCR598	cod liver	X	X	X		X	X		X
CARP-1	carp				X				X
BCR349	cod liver								X
BCR350	mackerel								X
BCR682	mussel								X
BCR718	herring								X

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CRMs for POPs in sediment

CRM	c-C	diox/furan	DDT	HCB	PCB
SRM1944	X		X	X	X
SRM1939a	X		X		X
IAEA383					X
IAEA408			X	X	X
HS-1					X
HS-2					X
BCR536					X
DX-1		X			
DX-1		X			

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No CRMs for:

- Toxaphene in biota and sediment
- Mirex in sediment
- Trans-chlordane in sediment
- Aldrin, endrin and heptachlor in biota and sediment
- POPs in water, air, human tissue, blood

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Interlaboratory Studies

Advantage: use of <u>blind</u> tests

- One-off Studies
- Stepwise-designed studies
- Proficiency tests

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Stepwise Designed Studies

- Standard solution
- Clean extract
- Unclean extract
- Real matrix

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Proficiency Tests: QUASIMEME

- Regular distribution of test materials (e.g. 2x per year)
- Direct report to participants
- Use of Z-scores

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Z-scores:

$$Z = (x_i - x_m)/s_b$$

$X_{i\ =}$ reported value
$x_{m\ =}$ assigend value
$s_{b\ =}$ target performance (st. dev.)

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Meaning of Z scores

- $|Z| < 2$ Satisfactory
- $2 < |Z| < 3$ Questionable
- $|Z| > 3$ Unsatisfactory
- $|Z| > 6$ Extreme Bias

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Other Interlaboratory Studies

- WHO-GEMS (5 proficiency tests trace metals and organochlorine pesticides)
- WHO dioxins and furans
- AMAP (human tissue and others)
- Norwegian Institute Public Health: dioxins and furans in food

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Quality of Data

- Guidelines on sampling and analysis (e.g. JAMP guidelines)

- % Accuracy: = 100 (|b| + 1.645σ) / μ

- Detection limits: 0.1 ng/kg - 1 μg/kg

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Quality of Data

- Only some POPs can be determined by *groups* of laboratories with sufficient accuracy to detect trends in the environmental concentrations of < 50%

- The use of expert laboratories may be beneficial for a number of POPs

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Data Presentation

- Check on Quality Criteria (recoveries, LRM.CRM, etc.)
- Flagging of data
- Discussion of data by QA/QC committee

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Data Communication *by Dr. Noriyuki Suzuki*

UNEP Workshop to Develop a Global POPs Monitoring Programme to Support the Effectiveness Evaluation of the Stockholm Convention

Data Communication

Data Communication
General Objectives

● Develop a common definition for "Data Communication"

– Wide variety of ideas could be implied by the word "Data Communication"

– Adopting a common definition will:

● Allow achievable goals to be established

● Avoid confusion during discussions

Data Communication
General Objectives

- Develop a warehouse of monitoring data that will be useful for the effectiveness assessment of the Stockholm Convention
    - Data warehouse containing monitoring data from Global Monitoring Network by UNEP
- Communicate with other Workgroups
    - Major impact from Effectiveness Assessment, QA/QC and others
    - Clear input of the needs for 'data communication' is essential for the fruitful and effective discussion

Data Communication
Background Paper

- Identification of objectives
    - Background
        - Effective data sharing to meet assessment needs
    - General goal
        - Developing a warehouse of monitoring data that meets the assessment needs and is technically feasible.

Data Communication
Collection and Use of Data

- Major topics may fall into the two areas
  - How to collect data
    - Which data elements, properties and information should be collected based on the assessment needs?
    - What types of data from various monitoring activities should be considered? (raw data, summarized data)
  - How to present and/or use data
    - Who are the users of the expected data warehouse?
    - How should data be presented to satisfy the needs of all users of the data?

Data Communication
General Goals for Discussion

- Data Collection
  - *Development of data and metadata structures for effective communication*
    - Identify necessary data elements, including measurement data and metadata
  - *Development of methodologies for collecting and storing all data from participating countries*
    - Electronic vs hard copy data
    - Data ownership issues

Data Communication
General Goals for Discussion

- Presentation and Use of Data
  - *Development of effective strategies to share information with the public*
    - How can we identify the user community?
    - How should data be shared?
      - Electronically (Internet, other media)
      - Written reports
      - GIS, Charts, Graphs, Raw Data
    - How do we address data ownership issues?

Data Communication
General Goals for Discussion

- Development of the Warehouse
  - *Development of strategies for building a data warehouse containing monitoring data with consistent properties and qualities*
    - Central system or dispersed system
    - Storing and presenting data in a consistent manner
    - Other topics concerning the practical building of a data warehouse

Data Communication
Impacts on Potential Strategies

- Assessment needs impact the strategies
- Defining the expected user community will impact the presentation methodology and ownership issues
- Technical feasibility also impacts the strategies, especially when we consider the possibility of collecting data from wide range of data sources

Data Communication
Review of Existing Databases

- Purpose
  - To take advantage of the successes of others
  - Only a few representative examples reviewed
- Problem identification for existing data communication systems
  - Results
    - Good examples of reporting formats
    - Metadata sometimes difficult to find
    - Some had too much emphasis on site and not enough on sampling results

Data Communication
Database Structures

- Clear definition of data elements is necessary to develop both reporting format and databases for the reported data
  - Identification of data elements that meet the requirements of the Convention
  - Identification of data elements that can be used for the sound scientific basis of the assessment
  - Ensuring that a practical and technically feasible approach is taken for collecting data and developing the database
- Major impact from requirements and needs of the Convention

Data Communication
Required Data Elements

- Which data elements are required to meet assessment needs?
  - Data elements
    - Numeric data from monitoring
    - Metadata, including information on methods, site, sampling and QA/QC
  - Type of data collation
    - Individual analytical results or summarized results?
  - Coverage of the data collation
    - Single scheme applied to all countries or combination of multiple schemes with region-specific coverage?

Data Communication
Required Data Elements

- What is the "core set" of metadata required to ensure that assessment needs are met
  - Variety of analytical methods, site selection criteria, sampling scheme, QA/QC practices and data handling schemes, are used in various monitoring programs
    - There may not be major differences between programs, however, minor differences may cause substantial difficulties for data sharing
  - Needs to define the "core set" of information for the sound usage of data from the expected databases

Data Communication
Technical Elements

- Numeric Data Properties
  - *Effective digit information*
  - *Unit information*
  - *LOD/LOQ information*
  - *Storing and reporting data outside of the LOD/LOQ*
- Discussions on choice of substances, definition of LOD/LOQ, handling data below LOD/LOQ have major impact on this topic

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Data Communication Metadata Elements

- *Analytical protocols*
  - How to specify the analytical protocols?
  - Method references, description of unit procedures in the methods, rough categorization of methods, etc.
- *Sampling site location*
  - Geographical location that can be processed in a harmonized way like GIS

Data Communication Metadata Elements

- *The nature of sampling site*
  - Categorization of the nature of sampling site that can be shared for the assessment needs
  - Text-based description may require key word descriptors
- *Sampling protocols*
  - Similar problem for analytical methods description

Data Communication
Metadata Elements

- *QA/QC practices*
  - How to describe QA/QC practices in the database a suitable format?
  - Acceptance of data by some clear criteria
- *Data Ownership*
  - How to acknowledge the ownership and intellectual rights of the data owner in the collation and storage process and output?
  - Ownership issues may differ depending upon the use of the data

Data Communication
Presentation Methodologies

- Impacted by the expectations of the user community
  - What are effective ways of data manipulation and/or presentation for the purpose of the assessment requirements of the Convention?
- Discussion items concerning presentation methodologies
  - Presentation and use of raw data
  - Presentation and use of summary data
  - Data exchange mechanisms and issues

Data Communication
Strategies for Developing the Warehouse

- Short term vs long term strategies
    - Planning a road map
- Distributed vs centralized
- Database structure
- Data warehouse installation
- Heavily dependent on the discussion output of the Workshop

Data Communication
Example Format

- Can we go to discussions on developing a standardized format (reporting and storing) within the scope of this workshop?
    - Table 1
        - Shows one example of a standardized reporting format for dioxins
    - This topic needs to be explored in technical details later, after discussing the general scope of standardized format in this Workshop

Data Communication Summary

- Major Discussion Topics
  - Develop a data structure (required elements)
  - Develop a metadata structure (required elements)
  - Develop strategies for collating data
  - Develop strategies for presenting data
  - Develop a data ownership policy

GMN Capacity Building *by Mr. Paul Whylie*

What is capacity building?

Paul Whylie
UNEP Chemicals

What?

Institutional Development
Communication facilities
Technological capability
Human resources
Legal mandate
Sustainability

What?

Institutional Development

- Should that be national chemicals management development?
- Administrative infrastructure
- Measured objectives
- Defined responsibilities
- Legal mandate

What?

Communication Facilities

- Internet, fax, telephone, mail
- Access to UN foreign languages
- Continuity
- Human resources

What?

Technological Capability

- Housing
- Hardware and software
- QA/QC
- Training

What?

Human Resources

- From 3 to 73
- Commitment – both sides
- Legally binding
- Remuneration

What?

Legal Mandate

- Legislation the 'ante'
- Coverage to NGOs
- Does the Stockholm bind

What?

Sustainability

- Cuts across all variables
- Particularly worrisome for developing countries
- Firm…but gentle approach
- Ongoing programme of assessment

Why is it undertaken?

WHY?

- Global assessment
- QA/QC
- Harmonisation/Comparability

Who is involved?

Who?

All Parties to the Convention

Who?

- State agencies and regulatory bodies
- What of research organisations?
- NGOs and industry?
- Ad hoc assessments of accidents/hotspots?

When does it occur?

When?

It is always ongoing!

Where is it done?

Where?

- Sources

- Transboundary transport

- Relative capability

- Existing infrastructure

Where?

MAP OF THE GEOGRAPHICAL REGIONS OF ASSESSMENT
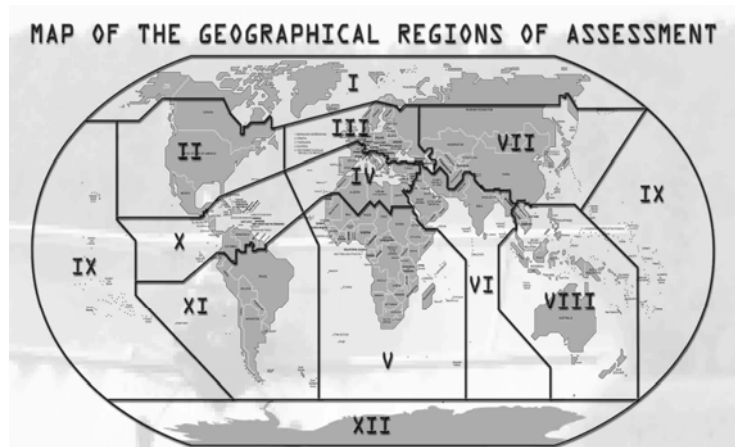
How is it done?

How?

- Complete assessment of status quo
- Financial resources committed - long term
- Regional approach
  - Common threads
  - Who does what for whom
- Endorsement by the COPs
- Technology transfer….

How?

…..Technology transfer

- Talk the same language
- Appropriate selection of technology
- Ongoing!
- "I work with Jack, you work with Jill"

How?

Ad hoc research/hotspot assessment??

Thank you

UNEP Workshop to Develop a Global POPs Monitoring Programme to Support the Effectiveness Evaluation of the Stockholm Convention

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Potential Role of Modelling in a Global POPs Monitoring Programme *by*
Mr. Frank Wania

UNEP

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

The Potential Role of Modelling in a
Global POPs Monitoring Programme

Frank Wania, University of Toronto at Scarborough

Stockholm Convention & Transport Modelling

Article 11 **Research, development of monitoring**
"encourage and/or undertake appropriate research, development,
monitoring and cooperation pertaining to POPs and, where relevant,
to their alternatives and to candidates POPs, including their:
- environmental transport, fate and transformation"

Article 16 **Effectiveness evaluation**
"provide itself with comparable monitoring data on the presence of
[POPs] as well as their regional and global transport"

Annex D **Information requirements and screening criteria**
"Environmental fate properties and/or model results that demonstrate
that the chemical has a potential for long-range environmental
transport through air, water and migratory species, with the potential
for transfer to a receiving environment in locations distant from
sources of its release."

Evaluating Effectiveness of the Convention

The Stockholm Convention is effective if exposure to POPs decreases.

This highlights the key importance of **time trends**.

Role of Modelling in Establishing Time Trends

"Models are not required to establish time trends"

However, model may:

- make sense of measured time trends
- suggest suitable media for establishing time trends
- help extrapolate measured time trends into the future

Making Sense of Measured Time Trends

observations concerning time trends could potentially be "conflicting" and/or confusing

Time trends are different:
- for different compartments (response times of different media to emission reductions is very variable)
- for different locations
- for different chemicals (due to differences in the change of emissions and in chemical properties)
- at different times

Making Sense of Measured Time Trends

Models can assist in understanding the variability in time trends with medium, location, chemical properties and time

Example 1: Differences in time trends of different PCB congeners
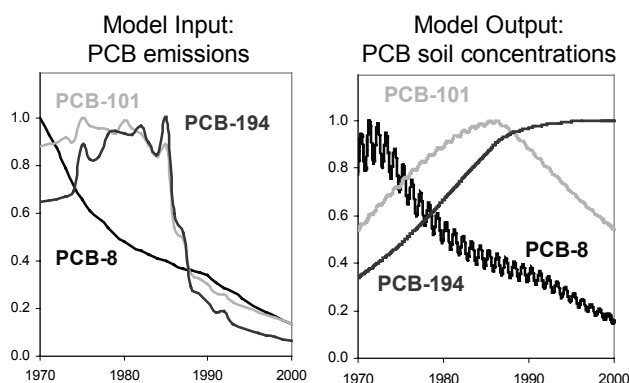
Making Sense of Measured Time Trends

Example 2: Differences in time trends in different regions

PCB-8 in sea water   PCB-101 in soil   PCB-194 in air
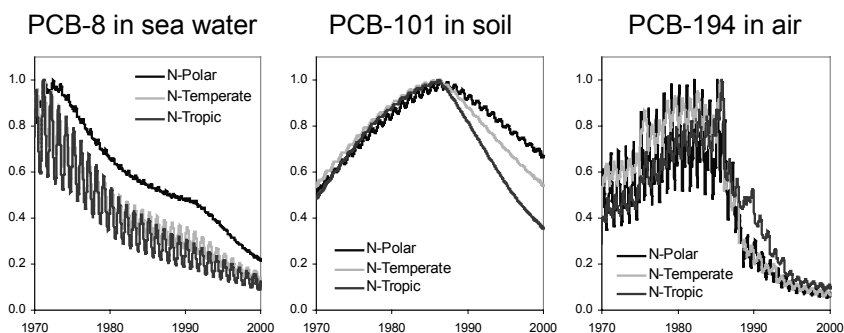
Real world time trends are more complex, because the environment is non-homogeneous in space and time

Time trends in biological sample are even more complex because of the spatial and temporal variability in bioaccumulation

Media Suitable for Establishing Time Trends

Model Input: global PCB emissions
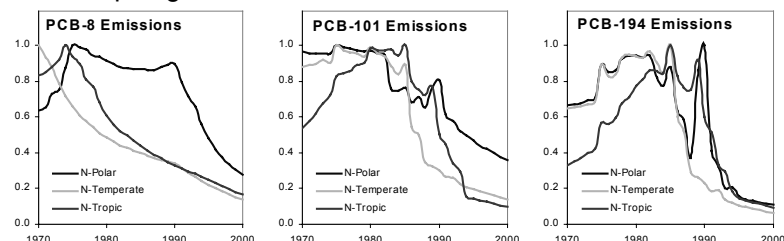
Model Output: PCB air concentrations
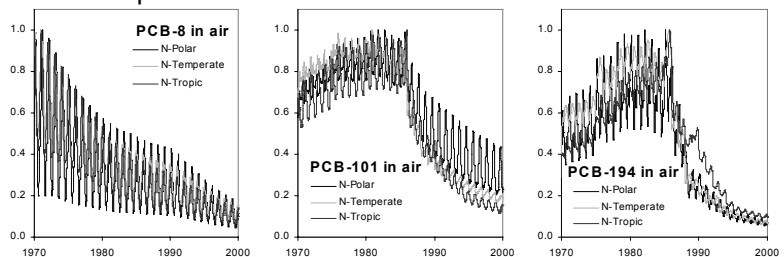
Media Suitable for Establishing Time Trends

Time trends in air concentrations follow closely time trends in emissions and thus should be useful for recording effectiveness of efforts to reducing emissions (though not necessarily exposure).

However, air concentrations undergo strong seasonal fluctuations, requiring either temporally highly resolved or time-averaged sampling.

Air monitoring also key in assessing regional and global transport.

Highly resolved model may assist in suggesting location of air sampling sites.

Extrapolate Measured Time Trends into the Future

Requires understanding of the dominant loss processes

■ Sediment burial
■ Deep sea transfer
■ Degradation other than air
□ Degradation in air

PCB-52

PCB-153
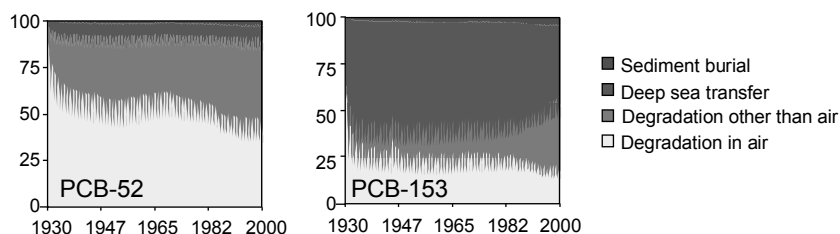
Prediction of global (or region-specific) clearance times
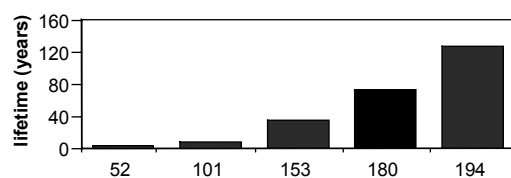
Wania and Daly, *Atmos. Environ.* **2002**, *36*, 5581-5593.

Regional and Global Transport of POPs

Questions Related to Regional and Global
Transport

- How much contaminant is transported from region to region?
- What is the origin of the contaminants occurring in a region?
- What is the destination of the contaminants originating in a region?
- What are the pathways of interregional transport?

These are all questions that can be addressed with
a variety of global and continental scale models.
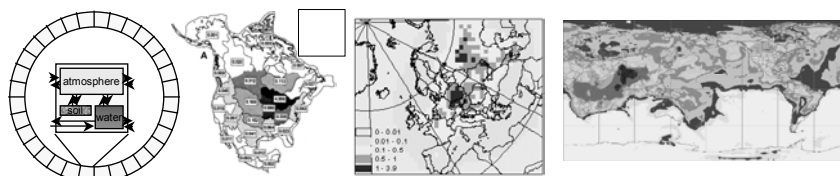
Regional and Global Transport of POPs

Relationship to monitoring is that model require data for evaluation in order to have credibility.

Different models require different data for evaluation.

Spatial and temporal resolution of model and measurements should be matched. A model may calculate at high spatial and temporal resolution, yet if there is no observational knowledge of the concentrations at such resolution, it is not refutable.

Models Assessing Long Range Transport Potential
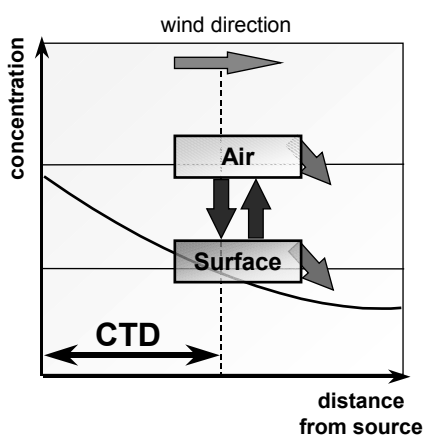
simple multimedia models can calculate measures of long range transport potential

relative size of such indicators allows one to discriminate, compare and rank different PTS in terms of their LRT potential
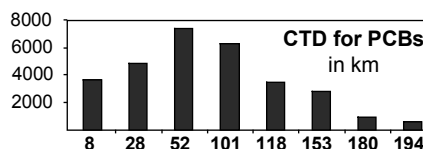
Models Assessing Long Range Transport Potential

Also these model should be evaluated!

Can the monitoring network provide data that can be used to evaluate LRTP assessment models?

e.g. comparing model-derived travel distances with half-distances derived from monitoring data

160

120

80

40

0

DDT
ng/sampler
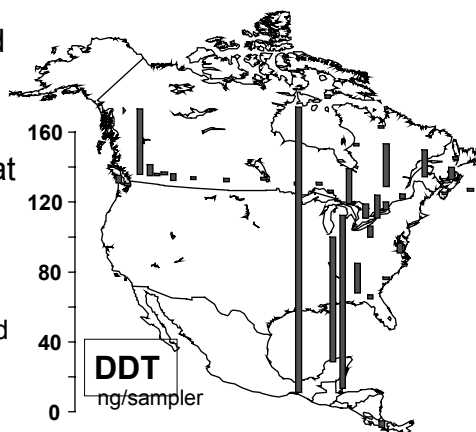
Summary

- Models may help to understand, explain, and extrapolate time trends in monitoring data
- Models may also assist in the planning of the monitoring network (type and location of sampling)
- Monitoring data may help to evaluate models
  - of regional and global transport
  - of long range transport potential assessment
- Models and Monitoring data need to be matched with respect to temporal and spatial resolution

A Potential Framework for Global POPs Monitoring *by Mr. Leonard A. Barrie*

THE GLOBAL ATMOSPHERE WATCH: A POTENTIAL FRAMEWORK FOR GLOBAL POPs MONITORING (WMO/GAW)

Leonard A. Barrie
Chief Environment Division, AREP, WMO
barrie_L@gateway.wmo.ch

THE WORLD METEROLOGICAL ORGANIZATION
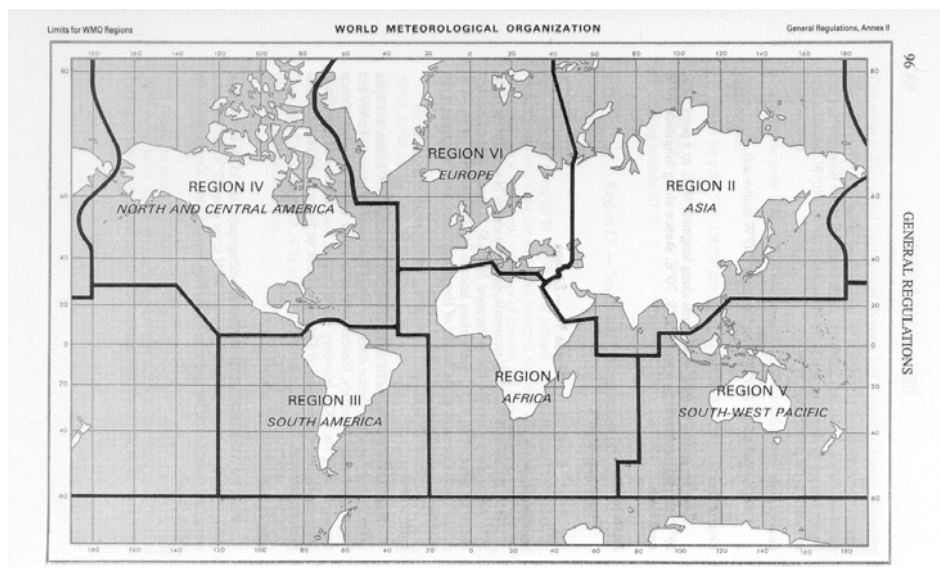
THE GAW MISSION

- **SYSTEMATIC MONITORING OF CHEMICAL COMPOSITION GLOBALLY**

- **ANALYSIS AND ASSESSMENT**

- **DEVELOPMENT OF A PREDICTIVE CAPABILITY**

SUPPORT OF INTERNATIONAL CONVENTIONS

MONITORING THEMES

- **Greenhouse Gases (CO_2, CH_4, N_2O, O_3, CFCs)**
- **Stratospheric Ozone** ⟵⟶ **UNEP**
- **UV Radiation** ⟵⟶ **UNEP**
- **Reactive Gases (CO, VOC, NO_y, SO_2)**
- **Precipitation Chemistry**
- **Aerosols**
- **POPs ……………..!!!!!!** ⟵⟶ **UNEP??**
- **Mercury…………..!!!!!!** ⟵⟶ **UNEP??**

WORLD METEOROLOGICAL ORGANIZATION
GLOBAL ATMOSPHERE WATCH GLOBAL NETWORK
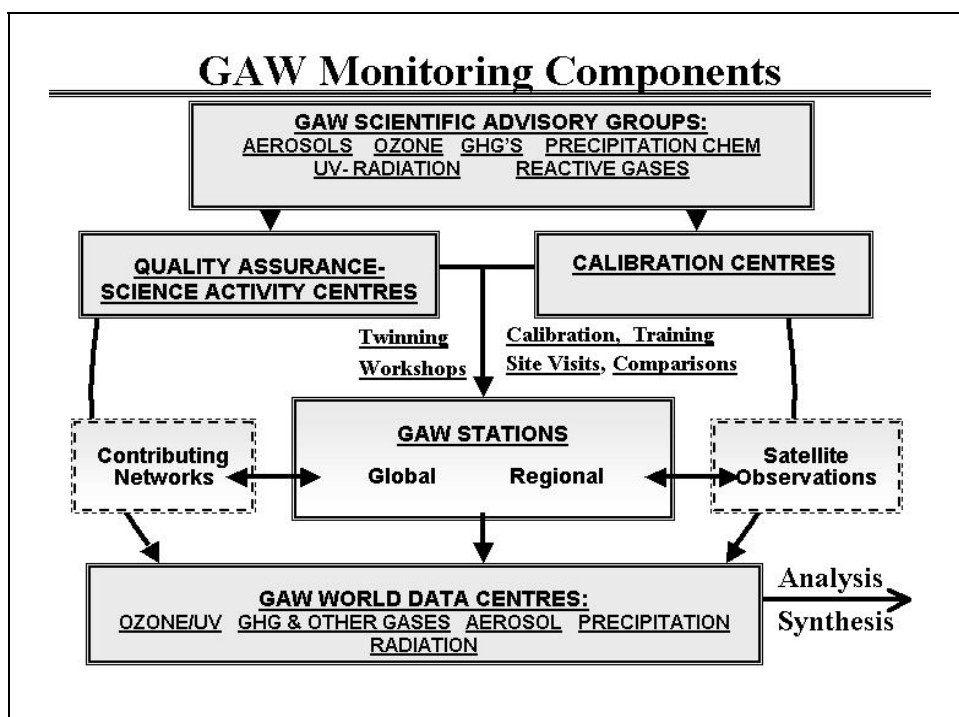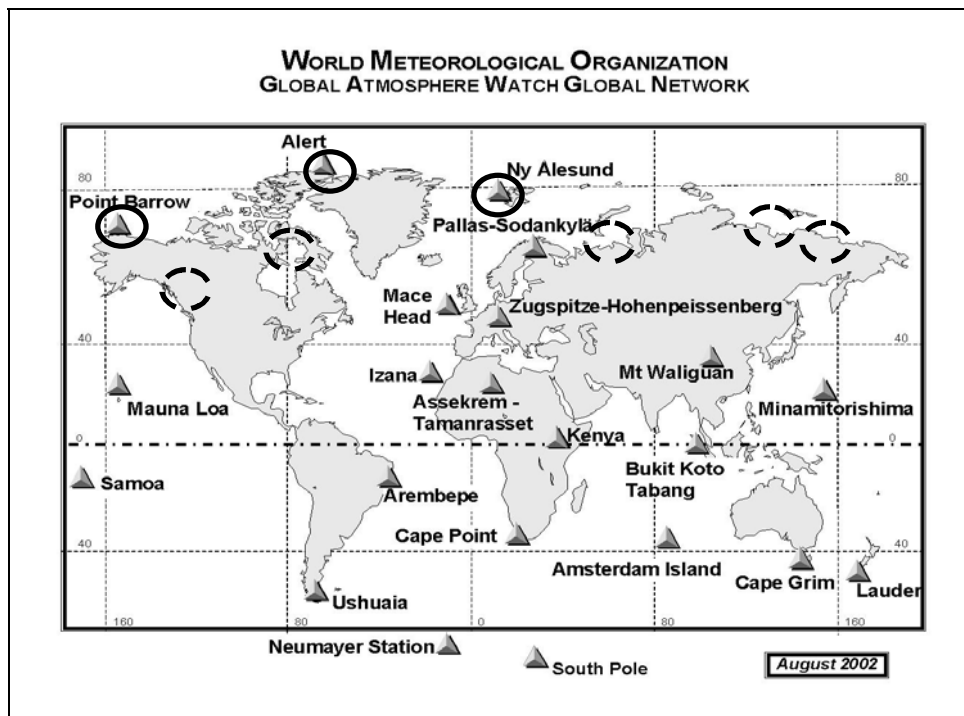
NORTHERN CONTAMINANTS
SAMPLER TAGISH YUKON

DUNAI ISLAND RUSSIA SITE
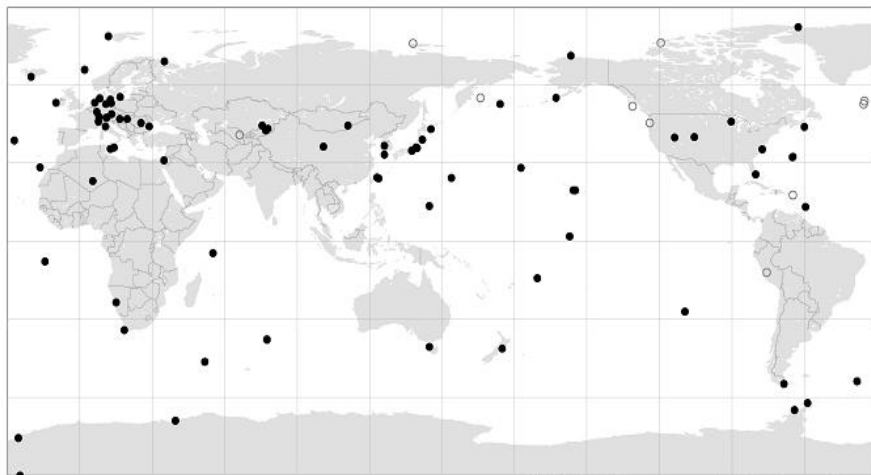
OZONESONDE NETWORK
IN 2002-2003: Data since at least 1999
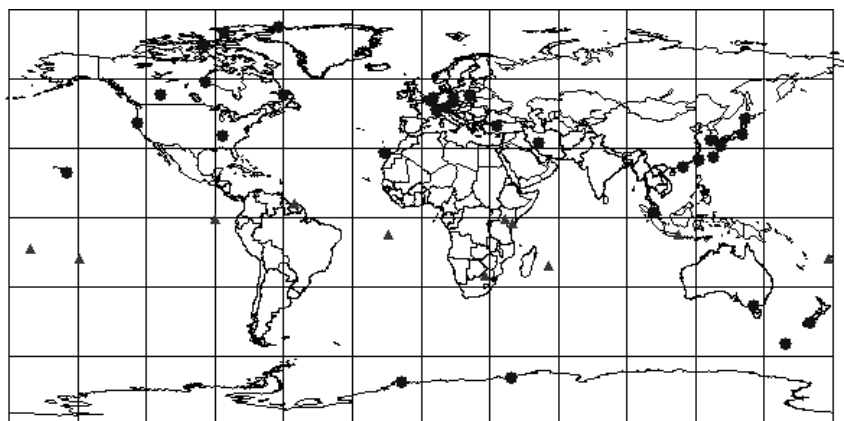
Network Ozonesondes   ▲ SHADOZ ozonesondes

Compliments of WOUDC, Toronto Ed Hare Manager

WORLD QA/CALIBRATION CENTERS

1. *In Situ* CO, CH_4, O_3 **EMPA, Switzerland**
2. CO_2 **NOAA CMDL USA**
3. **Total Ozone**   **NOAA CMDL USA**   <u>Dobson</u>
       MSC, CA   <u>Brewer</u>
       MGO, Russia   <u>M124</u>
4. **Ozone Sondes**   **FZ-Julich, Germany**
5. N_2O, **VOC**   **IMK-IFU Garmisch Germany**
6. **Aerosol physics**   **IFT, Leipzig, Germany**
7. **Aerosol optical depth**   **WORCC, Davos, CH**
8. **Precip. Chemistry**   **Suny Albany, USA**

WORLD DATA CENTRES

1. **Ozone and UV**   **MSC Toronto, Canada**

2. **GHGS**   **JMA Tokyo, Japan**

3. **Precip. Chemistry**   **SUNY Albany, NY,USA**

4. **Radiation**   **MGO St. Petersburg, Russia**

5. **Aerosols**   **JRC, Ispra, Italy**

Analysis and Assessment

ASSESSMENTS

- **Support Triannual Ozone Assessment ←→ UNEP**
- **IPCC (GAW data and modelling are used)**
- **UN-ECE Convention LRTAP ←→ EMEP**
- **!!! Stockholm Convention on POPs!!!**

Deviations (%) / Ecarts (%), 2001/10/16
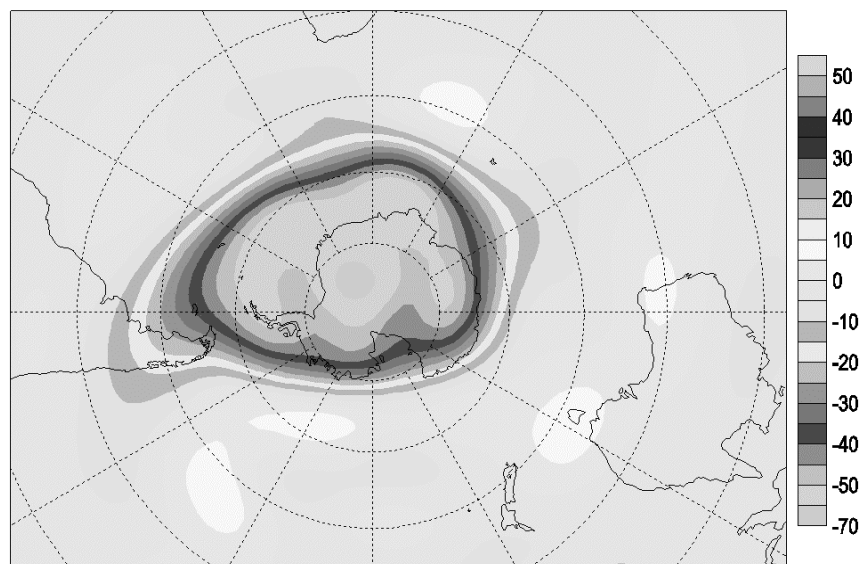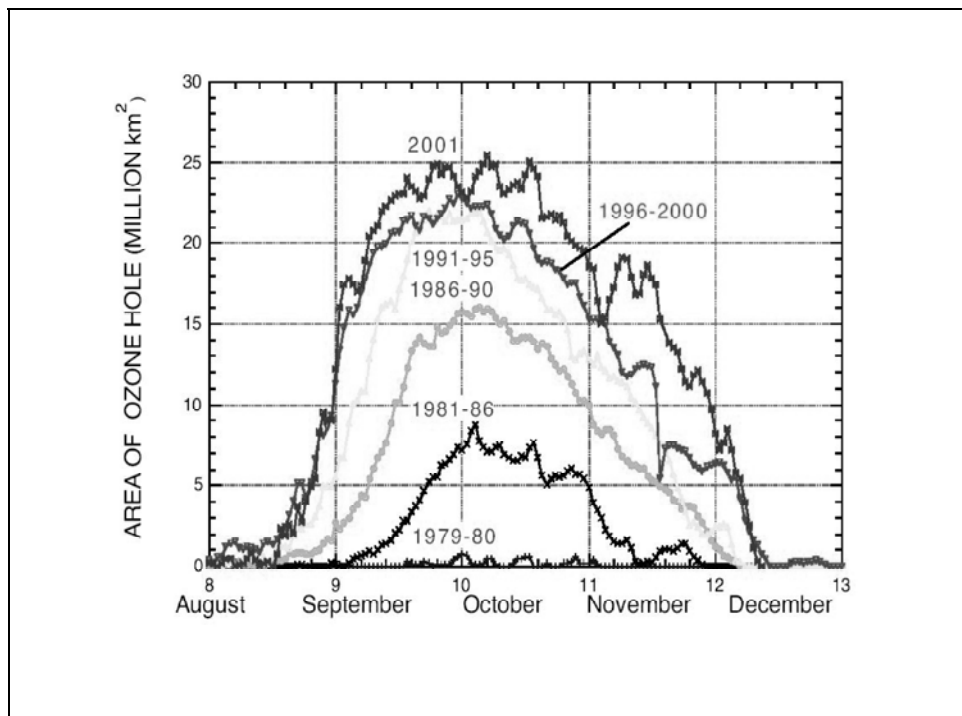
Development Of Predictive Capability

The Data Stream

The Products

QA Standards & Data Handling Protocols

Measurements

Data Assimilation

Data Archives

Reanalysis

4-D Distribution

Forecast: Weather or Air Quality
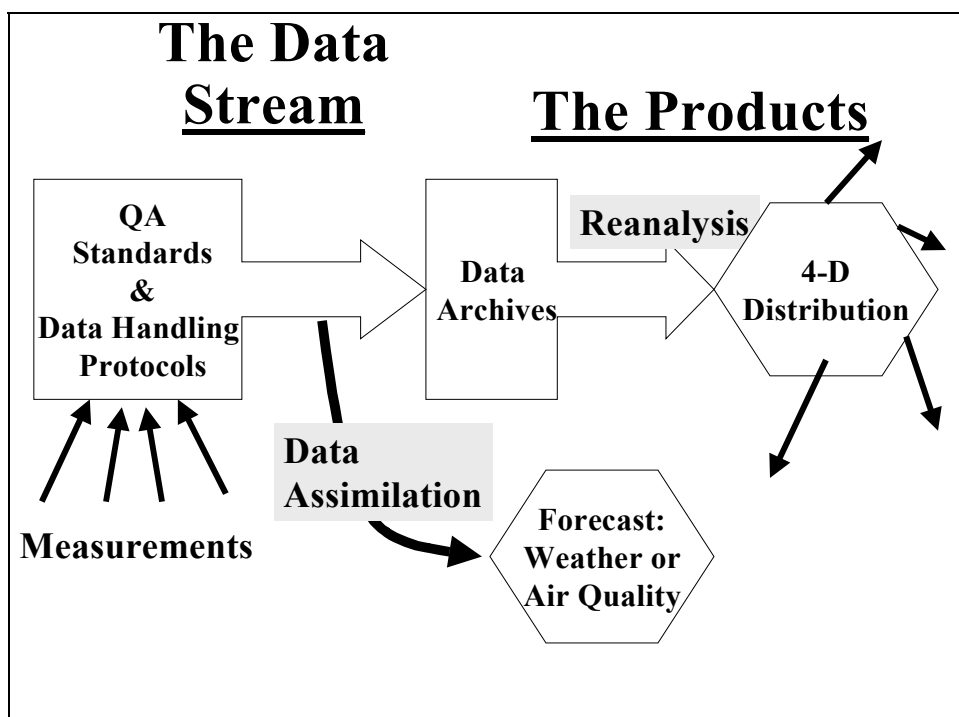
WORLD METEOROLOGICAL ORGANIZATION
GLOBAL ATMOSPHERE WATCH

No. 117
REPORT AND PROCEEDINGS OF THE WORKSHOP ON THE ASSESSMENT OF
EMEP ACTIVITIES CONCERNING HEAVY METALS AND PERSISTENT
ORGANIC POLLUTANTS AND THEIR FURTHER DEVELOPMENT
(Volume I)

organized by

Meteorological Synthesizing Centre East of EMEP,
State Committee on Environmental Protection of the Russian Federation,
and Chemical Co-ordinating Centre of EMEP
and co-sponsored by WMO

(Moscow, Russian Federation, 24-26 September 1996)

A contribution to the Convention on Long-range Transboundary Air Pollution

WORLD METEOROLOGICAL ORGANIZATION
GLOBAL ATMOSPHERE WATCH

No. 136

**WMO/EMEP/UNEP WORKSHOP ON MODELLING
OF ATMOSPHERIC TRANSPORT AND DEPOSITION
OF PERSISTENT ORGANIC POLLUTANTS AND HEAVY METALS
(Volume II)**
organized and sponsored by
Meteorological Synthesizing Centre East of EMEP and
World Meteorological Organization
in co-operation with the United Nations Environment Programme

(Geneva, Switzerland, 16-19 November 1999)

A contribution to the Convention on Long-range Transboundary Air Pollution

6. BACKGROUND PAPERS

Assessment Needs for The Stockholm Convention

Prepared by: David Stone
Indian and Northern Affairs Canada

ABSTRACT

Article 16 of the 2001 Stockholm Convention on Persistent Organic Pollutants (POPs) requires that the Conference of the Parties shall periodically evaluate the effectiveness of the Convention. This will include an evaluation of three elements: National reports; non-compliance information; and, an assessment of comparable environmental monitoring data on the chemicals listed in the action Annexes. This paper is concerned with the latter task. It attempts to identify key issues, which must be addressed when establishing arrangements for a framework to acquire and assess environmental POPs information necessary to support effectiveness evaluation. Three possible organizational options are analysed and a possible operational framework to move data through to assessment is proposed.

Introduction

This paper is intended to assist discussions at the "UNEP Workshop to develop a Global
POPs Monitoring Programme to support the Effectiveness Evaluation of the Stockholm
Convention."

Article 16 of the Convention requires that commencing four years after entry into force, the
Conference of the Parties (COP) shall evaluate the effectiveness of the Convention. In order
to do this, the COP shall, at its first meeting, begin the establishment of arrangements to
provide itself with comparable environmental monitoring data on the chemicals listed in the
action Annexes. Reports to the COP on monitoring are required at intervals to be specified
by the COP, but the Convention does not indicate how or by whom the reports will be
prepared, except that it is to be a responsibility of the COP.

The establishment of an appropriate monitoring capacity in areas where it does not already
exist will take two or more years to become operational. Furthermore the organization of an
assessment of the resultant information on global levels of persistent organic pollutants
(POPs) can be expected to require another two or more years. In order to ensure that the first
evaluation can be produced four years after entry into force, it is a priority that a clear
framework for the gathering of monitoring information and for its assessment be agreed upon
at the earliest opportunity. The specific focus of this paper is to review different strategies
that could be taken to establish such a framework. This has been undertaken by considering
the following elements:

1) Analyzing the boundaries of the monitoring and assessment task;
2) Briefly reviewing what can be learned from other international monitoring
    programmes;
3) Suggesting fundamental criteria for global monitoring which could assist organizers
    during planning and implementation;
4)   Reviewing organizational options in relation to the assessment needs;
5) Identifying minimum information needs;
5) Briefly considering the role of modeling;
6) Considering modalities for capacity building; and,
7) Proposing a possible operational framework to move data through to assessment.;

1) Analysis of the boundaries to the task

It is essential that the objectives of the global monitoring be clearly understood in order that
boundaries can be placed around what is required. For this it is necessary to return to the
Convention.

Paragraph 1 of the Article 16 states that the **Conference of the Parties shall** periodically
review the effectiveness of the Convention. Paragraph 2 describes how a component of this
evaluation will consist of the gathering of global information on POPs in the environment
(which for simplicity is here referenced as global POPs) and the subsequent assessment of

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this information. Reports are to be prepared for the COP. Paragraph 3 describes how this information will be one of three elements to be used for the purpose of effectiveness evaluation. The two other components are National Reports submitted pursuant to Article 15, and Non-compliance Information relative to Article 17. The latter two aspects are not the subject of the present exercise because they do not involve the early mobilization of technical resources, and are not concerned with the gathering and assessment of environmental information. However, their ultimate contribution in a complete evaluation of effectiveness will be essential.

- *Boundary Observation 1: The task to be undertaken is concerned with the gathering and assessment of information on POPs in the environment. It is not concerned with National Reports or with non-compliance, and it is not intended as a tool to detect "hot spots", since these would give a false signal as to how the regional and global environments are responding to the Convention.*

Paragraph 2 states that the **COP shall** have responsibility for establishing the arrangements to acquire the necessary monitoring information, but it is the **Parties** who **shall** bear responsibility for implementation. Section 2a makes it clear that implementation can be conducted on a regional basis which is clearly aligned with the stated purpose of documenting the presence of POPs "as well as their regional and global transport". The utilization of existing arrangements is encouraged. The Convention is silent on the possibility of implementation being achieved via individual national participation.

- *Boundary Observation 2: Implementation is a responsibility of Parties but this can be achieved through participating in a regional programme.*

The objective as described in paragraph 2 is to "monitor the levels of the chemicals listed in Annexes A, B, and C, as well as their regional and global transport". Measurement of levels alone will not be informative, but the detection of change over time (temporal trends) will be essential for effectiveness evaluation. The text does not prescribe that all Annex A, B, and C substances must be measured in all components of the sampling matrix. No mention is made of other chemicals, (e.g., possible candidates for inclusion in the Annexes), and although transport is referenced in a global context, there are no geographic boundaries placed around the assessment of trends.

- *Boundary Observation 3: It is obligatory only to consider the substances contained in the Annexes, but they need not all be measured in all components of the sampling matrix; and,*
- *Boundary Observation 4: Levels of POPs will be measured in order to detect temporal trends (essential for effectiveness evaluation). This could be given a regional focus, although it is required that a global context is included in relation to environmental transport.*

Article 11 is concerned with the research and monitoring which is necessary to attain a comprehensive understanding of such characteristics as the sources, movement, fate, behavior and toxicity of POPs in the environment. These activities can be conducted at any

level of organization (e.g. national, regional or global) and it is not restricted to the
substances listed in the Convention. There is no reporting link to Article 16, and this article
does not mention
Article 11.

- *Boundary Observation 5: The focus of the monitoring described in paragraph 2 of
  Article 16 is not to contribute to the science of understanding how POPs behave in
  the environment and it is not intended to aid in the preparation of dossiers for
  substances that are being proposed for addition to the Annexes. It is however
  possible that the monitoring activities may assist with these aspects, but this will not
  be reflected in the core level of the monitoring design.*

Paragraphs 2a and 2b of Article 16 make it clear that the implementation of Article 16 must
be sensitive to variations in capacity and to environmental conditions between Parties and
Regions. To some extent, this can be aided by the regional approach. However, there are
two immediately obvious implications. Firstly, differences in capacity clearly provide an
opportunity for strategic regional capacity building. Secondly, if there is to be a level of
global uniformity, thought should be given to identifying the minimum information needs
that would inform the COP on whether levels of POPs are decreasing in the environment
(temporal trends) and whether there are features of their transport which should be considered
in effectiveness evaluation. In using the terms "comparable monitoring data", and
"harmonization of methodologies", together with promoting the use of "existing monitoring
programmes and mechanisms", paragraph 2 of Article 16 is clearly acknowledging the
importance of such characteristics as data quality assurance and quality control (QA/QC).
This will be an issue with every parameter selected for study, and its magnitude will be
related to the number of parameters studied and to the number of participating laboratories.

- *Boundary Observation 6: Differences in capacity within and between regions provide
  opportunities for strategic regional capacity building focused to ensure a capability
  to detect regional trends; and*

- *Boundary Observation 7: The challenges of obtaining comparable monitoring data
  (inter alia harmonization, QA/QC) and of the world mosaic of capacity suggest the
  wisdom of identifying the minimum data set necessary to inform the COP on trends.*

Article 16 does not specifically exclude non-parties from contributing information. Once the
Convention has entered into force, the number of Parties can be expected to grow, and
therefore it would be shortsighted to design an initial programme that does not take this into
account. It is proposed that countries that have signed the Convention, but are not yet Parties,
should be allowed (and encouraged) to provide information which conforms with whatever
arrangements may oversee all contributions of information (e.g. QA/QC), if they are prepared
to do so.
- *Boundary Observation 8: Non-parties are encouraged to contribute acceptable
  information to the programme if they wish. However, countries participating in this
  way would be "passive" contributors and would not be able to take part in decision
  making, or be members of the writing team for the periodic assessments.*

2) What can be learned from other International Programmes

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 is not yet in force) (UNECE 1998) contains Article 8 which requires
that Parties **shall encourage** research and monitoring on POPs in the environment. It does
not specify who will conduct the work, although this responsibility is in part being taken up
by EMEP (e.g. EMEP 2002 (b), an organization which formally does not embrace the entire
geographic area of the Convention. EMEP is making progress to document trends in
association with the heavy metals Protocol under the LRTAP Convention (EMEP 2001). It is
interesting that Article 8 looks towards substances that may be candidates for addition rather
than for substances already subject to measures. Article 10 of the Protocol requires that
Parties shall review information supplied by Parties, EMEP, and other bodies. It is therefore
possible to envisage that a review of some aspects of effectiveness may emerge as procedures
evolve under the Protocol.

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 Hesinki Convention (e.g. HELCOM 1996, and Roots 1996) and the Joint
Assessment and Monitoring Programme under the 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 present 12 Stockholm Annex 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 are the Global
Environmental Outlook (UNEP 1999); the various marine environment assessments
undertaken by GESAMP (eg GESAMP 2001); and the assessments undertaken for the
circumpolar Arctic by the Arctic Monitoring and Assessment Programme (AMAP 1998), and
for Europe
(EEA 1998).

Other programmes have been established to provide a regional or global survey of the levels
of certain POPs in particular media. These include for example, 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 PCBs, PCDDs and PCDFs) in food and in human milk (GEMS FOOD 1997, GEMS FOOD 1998, van Leeuwen and Malisch. 2002).

Finally, it is instructive to review the organization and management of the recently made available Regionally Based Assessment of Persistent Toxic Substances (GEF/UNEP 2000/3). This project, which has been conducted through the Global Environmental Facility and UNEP Chemicals was not concerned with monitoring but aimed (inter alia) to provide a regionally based assessment global of persistent toxic substances in the environment, their concentrations and impact on biota, and their transboundary transport. It therefore faced many of the challenges that lie ahead for the global monitoring of POPs. A series of regional assessments were planned, and produced within the regions by teams of regional experts, each following an over-all global strategic framework of procedure (GEF/UNEP 2000/3).

Although the above programmes did not embrace a task of the nature demanded by Article 16 of the Convention, certain lessons have been extracted from the literature and from personal contact with the programmes noted. Some of the most important criteria appear to be:

- *The essential nature of inclusiveness and transparency in all aspects of the programme design, conduct and in the assessment process*. Failure here leads to an escalation of difficulties, which can lead to a lack of acceptance of the assessment.

- *That the objective of the task must be repeatedly emphasized*. Without this being done, programmes are in considerable danger of straying off course. It appears to be especially important in decentralized programmes.

- *The value of clarity of: design for the sampling activities; of expectations for standards of analytical performance; and of arrangements for QA/QC.* Some programmes failed to give these aspects sufficient attention and most report difficulties in the assessment process for which they were the root cause.

- *That simplicity is beautiful*. This lesson appears to concern all aspects of monitoring and assessment programmes. For example: it applies to the sampling matrix: to arrangements for analysis; for QA/QC; and even to protocols for preparation of the assessment. Only do what you have to do in order to complete the task and there is a reasonable probability that you will meet with success.

- *That arrangements must have a high expectation of being sustainable*. This is best achieved by simplicity and it is closely related to cost effectiveness. It is particularly important with respect to analytical arrangements and to the sampling matrix. New elements can always be added to a matrix but in practice it is usually difficult to remove an element.

- *That if implementation is performed using a regional approach, the regionalization should reflect what will best serve the needs of data gathering and assessment.* A large number of international organizations have a regional structure. It will be instructive to review these pre-existing arrangements but there should be no pre-

conceived notions as to the adoption of any existing scheme.

- *The value of plasticity*. This is referring to the programmes ability to evolve over time in order to respond to the needs of the Convention. Plasticity is again enhanced by simplicity of the original design.

- *Use a tiered approach to preserve simplicity while allowing the programme to explore new areas*. This is usually implemented by the design including core activities, upon which are superimposed one or more levels of supplementary or voluntary elements. For example, under Boundary Observation 5, it was proposed that the monitoring "*is not intended to aid in the preparation of dossiers for substances that are being proposed for addition to the Annexes*".   However, in examining the effectiveness of the Convention, Parties interested in moving an Annex B substance to Annex A, or to modify the emissions for an Annex C substance, may wish to add a second tier of voluntary enhanced monitoring to better appreciate control options.

- *The necessity for a clear understanding of data ownership*. Intellectual property difficulties have arisen when participants were confused on these issues.

- *The mediation of QA?QC and of data availability has frequently been achieved using "thematic data centres"*. Frequently these are pre-existing and operated by other programmes and organizations.

- *The need for a uniform understanding by all members of the assessment teams on the objectives of the task*. Several programmes reported difficulties on this aspect, despite the publication of comprehensive guidance documents.

- *The necessity for clear accountabilities for those involved in the assessment*. This is particularly important when the assessment is decentralized. In addition to guidance documents, a cental role to ensure compliance with the guidance and with timelines appears to be unavoidable.

- *The importance of assurance of unencumbered access to data for the assessment.*
  Several programmes reported difficulties in gaining data access at the time of
  assessment, particularly with respect to supportive information (e.g. age or sex of
  species from which samples may have been taken).

- *The most common mode used for the preparation of an assessment document is to use
  an authorized team of experts*. They may be designated by countries or a
  recommended panel of experts may then be approved.

**3) Suggesting fundamental criteria for global monitoring to which organizers could
refer during planning and implementation**

The boundary observations from Section 1 and the "lessons learned" from Section 2 have
been combined in the appendix to provide a list of criteria which may assist decision-making
during the design and implementation of the programme.

4) Reviewing organizational options in relation to the assessment needs

An important early step in the planning process is to recall the objective of the activity and to
consider how the assessment may be conducted in order to achieve that objective. The
appropriate selection of such details as site selection and environmental media matrices,
should be driven by a clear understanding of how the information will be used in the
assessment and of the practical implications associated with various choices of delivery and
organization.

We are being asked to detect temporal trends in levels and to do this we must have data that
can be compared. This requires a decision on identifying the geographic scale over which we
will seek comparable data. The nature of this decision has fundamental implications, since it
not only defines the nature of the ultimate product but also suggests options for organization.
Although a number of geographic scales for assessment and accompanying organizational
structures are possible, only three have be analysed below:

**4.1) *Option 1: National.   What are the implications of the primary unit of organization
being at the national level?***

Under this option, every party would be responsible for collecting and analyzing POPs
according to an established globally uniform procedure. The data could be assessed
nationally, and the assessment alone made available to regional and/or global assessment
teams, or the data alone could be provided to such teams. There would be a hierarchy of
assessment reports, national, regional, and global.

Advantages:
- It is inclusive. All Parties would be involved.

Disadvantages:
- Many countries will not have the laboratory analytical capacity to support this approach;
- Even if capacity building resources to provide the required infrastructure can be made available, it is very doubtful that the level of work required would be sufficient to sustain that infrastructure over time;
- The quality assurance and quality control implications necessary to ensure the comparability and harmonization called for in Article 16 would be daunting, regardless as to whether the assessment is conducted regionally or nationally;
- Lack of data comparability will prevent meaningful comparison of national tend assessment reports and will not be capable of supporting an analysis of regional or global transport; and,
- In contrast to regional and global options, this approach is not indicated in Article 16 of the Convention, and it would not be able to make use of existing programmes and mechanisms as also outlined in the Convention.

4.2) *Option 2: Global. What are the implications of the primary unit of organization being at the global level?*

Under this option, all data within a unit of the sampling matrix would have global comparability, thus allowing for the product to include a true global assessment. A global coordinating unit would (after consultation with parties) ask certain parties and international organizations to collect data according to an agreed upon matrix and using globally standardized collection methodology. The samples would be sent to a very small number of accredited laboratories for analysis which would (in all probability) often not be located in the same region as that from which the samples were taken. The sampling would provide data that can be compared over a global scale. A global team would conduct the assessment, that could be presented in both regional and global formats.

Advantages:
- This approach affords the greatest opportunity to achieve global harmonization of methodology. The small number of participating laboratories involved would provide the greatest opportunity to deal with the quality assurance and quality control issues of the data;
- The potentially high level of data comparability resulting from global harmonization of methodology and high levels of QA/QC will enable:
  1) a global assessment of temporal trends to be undertaken; and,
  2) potentially support an assessment of regional and global transport.
- Utilization of existing regional and global programmes and mechanisms is possible; and,
- This approach could be cost effective, since it would primarily use the existing global inventory of analytical laboratory infrastructure already linked through established data comparability networks.

Disadvantages:
- This approach will be very demanding in terms of data comparability, since all data from the same media must have global comparability;
- By using primarily the existing global analytical infrastructure, this approach offers a very limited scope for capacity building;
- The centralized organizational nature of this approach creates a wide distance between Parties and the conduct of the work. This would not be inclusive and could have the potential for a serious lack of ownership between Parties and the assessments and subsequent effectiveness evaluation;
- It would be a challenge for this approach to fully accommodate regional differences in the environment and in capacity;
- Although this is the only approach examined here that offers a good potential for leading to a comprehensive global assessment, Parties may have a greater interest in seeing regional assessments.

4.3) *Option 3: Regional. What are the implications of the primary unit of organization being at the regional level?*

Under this option, all data within a unit of the sampling matrix would have assured regional comparability, thus allowing for the product to include a series of regional assessments. A global coordinating unit would establish a guidance document for the collection of data according to an agreed upon matrix and using standardized collection methodologies. Regional coordinating and assessment nodes would then organize the implementation of the guidance document in each region, taking into account regional environmental conditions and capacity. The regional implementation would place the responsibility for sampling at the national level, but to the maximum extent possible it would utilize regional resources for analysis and assessment. Regionally appropriate elements of existing regional and global existing programmes and arrangements would be integrated into each regional implementation plan. The series of regionally produced regional assessments would report on regional temporal trends. A global assessment would also be produced, which would consist of a summary of the regional assessments, but it would not attempt comparisons of data from one region to another. This approach could also have the potential to support a series of comprehensive studies on intra-regional POPs transport, but because of the lack of harmonization between regions, inter-regional transport assessment would be limited to such techniques as back trajectory analysis.

Flexibility should be applied in deciding upon how the world may be divided into regions and the criteria for defining a region could vary from region to region. It could reflect earlier arrangements: bio-geophysical conditions; economic arrangements; or simply reflect the comfort of a group of countries to work together.

Advantages:
• Regional organization reduces the distance between Parties and the conduct of the work and therefore could encourage a sense of ownership between Parties and the assessments and the subsequent effectiveness evaluation. It could strike a balance between practicality and inclusiveness;
• Each regional node would be able to accommodate regional differences in the environment and capacity, while still following the global guidance document;
• The number of participating laboratories involved within each region could be reduced to levels which would help maintain methodology harmonization and data quality assurance and quality control to a standard capable of supporting a regional assessment;
• The regional level of data comparability resulting from regional harmonization of methodology and regional management of QA/QC will enable:
   1) a regional assessment of temporal trends to be undertaken; and,
   2) support an assessment of regional transport.
• This approach includes many opportunities for cost effectiveness, since it could use existing regional and analytical laboratory infrastructure whenever it is available as well as the regionally relevant elements of global programmes; and,
• This approach offers substantial scope for the development of a shared capacity in regions. If this capacity is well organized, it should be possible to ensure that the work load in laboratories can be sustained, and that redundancy in capacity will not be created.

Disadvantages:
• The regionalisation of QA/QC implies that this approach would:
   1) not be suitable if an intent for the assessment is to compare data from one region to another. However, it is perfectly possible to envisage that Parties may have a greater interest in a series of regional assessments for the evaluation of effectiveness, than in a single stand alone global assessment; and,
   2) not be be suitable for the support of comprehensive studies on intra-regional POPs transport. Work of this nature may be limited to such techniques as back trajectory analysis. If this limitation is considered to be critical for the needs of the Convention, it is possible to envisage that special global arrangements may be possible to deal with these data needs while still maintaining an over-all regional organizational focus.
• Care would be necessary to strike a balance between the provision of firm global guidance to ensure the maintenance of global standards and to guarantee that assessments will be produced which will enable evaluation of the effectiveness of the Convention. This must be achieved without eroding the benefits of placing the main responsibility for implementation at the regional level; and,
• It is possible that some regions will require outside assistance at one or more stages (planning, implementing, and assessment).

5) Identifying minimum information needs

A discussion on the nature of the sampling matrix (matrices) can be found in the companion paper on "Site Selection, Matrices and Sampling Techniques".   However, some general observations are included here.

Deciding upon the basic nature of the sampling matrix is not a straight forward task but it can be simplified by close adherence to the text of paragraphs 1 and 2 of Article 16. The implications of this text were explored in developing "boundaries" as described in section 1 above. Further assistance can be taken from reviewing features found to be important in other monitoring

programmes, some of which were briefly reviewed in section 2.   These two sets of information have been combined in the Appendix, and used as a basis for the following suggestions;

- Simplicity leads to a considerable number of advantages including sustainability. The effectiveness of the Convention could be evaluated using a very small number of sample types. It is proposed here that the primary trends of interest to the Convention are related to:
  1) Air: to indicate early response to changes in releases of POPs, and to support statements on regional and global transport;
  2) An indicator of human exposure (e.g. maternal blood or breast milk);
  3) An indicator of upper food chain biomagnification (e.g., a representative carnivore); and possibly,
  4) An indicator of the source of human exposure (e.g. a predatory fish species heavily used as food.
  It is therefore proposed that these form the basic core of media to be monitored. The list could be elaborated to another tier of complexity, but such additions would not be considered as essential. Their contribution should be evaluated on their potential to add valuable trend detection capability or to enhance the global transport component, rather than on their importance for understanding the behavior of POPs in the environment.

- It will be extremely difficult to achieve global biotic data comparability (with satisfactory QA/QC). Therefore the programme should strive for regional uniformity as much as possible. For these reasons, the primary assessment would be most achievable if conducted at the regional level.

- Only the substances included in the Annexes to the Convention will be monitored, but they need not all be monitored at all locations. A strategy should be developed to optimize effort with productivity and costs. The Convention may also have more interest in Annex B and C substances than in the substances listed in Annex A.

- It will be impractical to achieve a representative sample for a region. It is therefore

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important to instead be confident that the samples collected at a sampling site are representative of that site in order that meaningful conclusions can be drawn on temporal trends. If this can be assured, the programme will have the ability to provide valuable information on trends for that sample set.

- It may not be essential to achieve a uniform spread of sampling sites over a region. However, it is important that there be a globally agreed common rationale for site selection and that sites are located outside of the influence of local sources. It is not necessary that the three or four media proposed above be sampled at precisely the same locations since the objective is not to explain ecosystem contaminant transfer. However media should share common bio-physical conditions. This leads to the proposal that the minimum number of sampling stations need not be large, although a number is not indicated here because it will depend upon the size and heterogeneity of individual regions.

- Air monitoring stations serve a double purpose, since they inform both on tends over time and on regional and global transport. A carefully designed sampling strategy will be required to match sampling with expectations for the assessment. Elements to consider include:

  1) Deciding whether the goal is to integrate concentrations over a long period, and or, to record the frequency and magnitude of pulses of contaminant laden air;

  2) Interpreting the Conventions expectations concerning regional and global transport. If models are used as a tool for this task, data requirements will tend to be high, but less so if a back trajectory approach is taken;

  3) For global transport, global harmonization and QA/QC will be necessary (in contrast to this having only a regional dimension as concluded above for biotic media), and supportive meteorological information will be required. Thought should therefore be given to co-locating at existing sites with supportive meteorological infrastructure (e.g. World Weather Watch coordinated by WMO); and,

  4) Reviewing opportunities to intensify sampling effort by using a mixed sampling strategy of active and passive samplers.

- The conduct of sampling of human material is complex and involves ethical, cultural, and religious issues. The first step should be to ascertain the capacity of a combination of existing arrangements including those of GEMS/FOOD (GEMS/FOOD 1998) to meet the needs of the Convention. However, existing programmes have been designed to address other needs and if they are to be used as part of the global POPs monitoring, we must be satisfied that they can also satisfy the objectives of Article 16. For example, can the variability of POPs concentration in a breast milk during a "feed" and during lactation be sufficiently accounted for?

The over-all conclusion is to suggest that the objectives of Article 16 can be achieved with a modest sampling matrix and a modest number of stations within each region.

5) The role of modelling

Modelling has played a very significant role in the over-all effort to better understand how several families of pollutant behave in the environment. In some cases, modelling has also been an essential tool within the operational framework of international control agreements. A striking example is the use of models to enable the critical load/critical level approach taken in the more recent acidification protocols under the Convention on Long-range Transboundary Air Pollution (e.g. EMEP 2002(a)). The critical load/critical level approach was not pursued in the LRTAP Protocol or the Stockholm Convention because of the complex intercompartmental partitioning dynamics of POPs in the environment. Nevertheless, POPs modelling continues to make significant contributions to knowledge on how POPs move through and partition within the environment (e.g. Shatolov 2001). However, this work is perhaps more at the level of research and development, rather than presently being a proven tool for a task such as "effectiveness evaluation". OECD (2002) has recently published a comprehensive review of the further potential of models to assist in the identification of priority substances to be added to existing agreements such as the 1998 LRTAP POPs Protocol and the Stockholm Convention.

There is no doubt that modelling activities of the nature described above are legitimate activities to be undertaken with respect to Article 11. However, is it necessary that new modelling activities be initiated or undertaken to enable the preparation of the periodic assessments required under Article 16?   This author is not qualified to provide a comprehensive answer to the question but the following observations are offered:

- It is not the objective of Article 16 to understand the environmental behaviour of POPs;
- Modelling from existing models may be useful in helping to establish where air monitoring sites should be located but is unlikely to contribute to sample site selection for biological media;
- The detection of temporal trends is not dependant on modelling;
- The projection of temporal trends into the future would require modelling, but this is not specifically called for in Article 16. It should be born in mind that the COP may at some time in the future request such projections in order to estimate the time period over which change could be expected to occur;
- Article 16 is not clear as to expectations concerning the statement in paragraph 2 "regional and global transport". As noted above, the scientific community has developed a variety of tools that can assist in demonstrating the long-range transport of POPs. Many involve models (e.g. Shatolov 2001; and as summarized in Scheringer and Wania, 2003; OECD 2002; and AMAP 1999) but others employ back trajectory analysis (e.g. Bailey
- et al 2000). It is quite probable that the assessment teams will use a variety of these tools as they are available at the time of assessment production; and,

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• During negotiation of Article 16, negotiators were extremely cautious with respect to costs. Therefore it is important that in developing arrangements for implementing Article 16, new modelling activities to service the assessment should only be undertaken if such tools can be shown to be essential for effectiveness evaluation.

Since modelling as a tool for assessment is most likely to be employed for the purpose of commenting upon "regional and global transport", perhaps the next step is for a "mock transport assessment team" to identify a range of practical products for this component of the assessment and to indicate the tools they would require to complete the task at both a regional and global level. In other words, the question should not be "what is the role of a particular tool (i.e. modeling)", but rather what is the job to be done and then what are the tools that would be required.

6) Capacity building

A separate paper has been prepared to discuss capacity building and the topic is commented here only in the context of the needs of an assessment process. Once it has been designed, the operation of a global monitoring programme for POPs will include three basic components: sample collection; sample analysis; and assessment. It can be expected that technical capacity to participate in the sampling will exist in all regions. Furthermore, the recently completed Regionally-Bases Assessment of Persistent Toxic Substances has recently successfully completed 12 regional assessments using regional resources (GEF/UNEP 2000/3). However, it is probable that there will be wide differences between regions in terms of analytical capacity. In most regions, the majority of countries may have the capacity to analyze for many of the present twelve Annex substances although it is possible that these facilities may not be accessible for the purposes of the global monitoring programme. In a number of regions, it is probable that there will be a very limited capacity to analyse for polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans (PCDD/PCDF), for coplanar PCBs (should it be decided to report PCBs in this way), and for toxaphene.

In Section 4 above, the advantages and disadvantages of selecting different levels of geographic scale for the sampling, analysis, assessment and the supportive organizational arrangements were reviewed. In summary, Option 1 (National) is not cost effective and is clearly not indicated from the text of Article 16. Option 2 (Global) would lack inclusiveness, is very demanding of data quality, and is again not indicated by Article 16. The most practical approach is probably one similar to Option 3 (Regional), which fully utilizes existing regional capacity while also offering substantial scope for the development of shared capacity in regions where such capacity does not already exist. Recalling the combining of "Boundary Observations"with "Lessons Learned" from sections 1 and 2 above into the criteria presented in the Appendix, it could be concluded that a capacity building strategy should include the following:

• aim to ensure that within each region, there is at least one facility with capacity to analyse the most challenging Annex substances;
• recognize that for such a facility to be sustainable, it must have work to do. The

creation of redundant capacity will be counter productive and probably lead to non-sustainability;

• recognize that other laboratory facilities in a region may have adequate capacity to analyse for the less demanding Annex substances. They should be used if they can be made available to the programme;

• note that for all participating laboratories, an adequate system must be put in place to ensure regional comparability of data (including QA/QC); and

• note that the desire to ensure inclusiveness will lead to an increase in the number of participating laboratories, but this will also lead to an increasing challenge in order to maintain data comparability.

From these considerations it is suggested that the development of a tiered capability within a region offers distinct advantages. Under such a scheme, all Parties would contribute samples and expertise to conduct the assessment, a number of Parties would also contribute analytical services for all but the most challenging compounds, while a minimum of a single laboratory located within each region would conduct all of the more challenging analyses for that region. This type of approach has been cost effect and performed well in regional monitoring programmes involving for example, North America, northern Europe, and Russia (AMAP 2002). It enables all participant Parties to share in technology enhancement, but recognizes the advantages of centralizing the most advanced analytical capacity at regional nodes.

Since the development of regional capacity will be vital for the success of a global monitoring programme, it is important that there is a good degree of confidence in the arrangements to be established. It is therefore suggested that it may be a priority to test whatever arrangements may be decided upon in one or two regions before the Convention enters into force. This (these) "pilot project(s)" would enable valuable practical lessons to be learned on how to approach and implement the monitoring framework and to put into operation a capacity building initiative. The resulting experience could then be applied to the development of capacity in other regions.

7) A possible operational framework to move data through to assessment

The intent of the preceding sections of this paper has been to review the needs of the environmental POPs monitoring component of Article 16, and to expose some of the most crucial issues that must be borne in mind when developing an operational framework. In this section, thoughts are drawn together from that review in order to suggest a potential framework. The review of organizational options (Section 4) indicated that the optimum approach is likely to be one built primarily around a series of regional assessments (Option 3). The following framework is therefore suggested.

a) A global advisory/steering group would be set up to oversee the development the framework. Membership would include a mix of scientists and bureaucrats from the Parties

together with international, industry and NGO organisations that may play a significant role in the work.

An initial task for this group would be to decide upon how the world may be divided into regions. Flexibility and practicality should drive the criteria used for this purpose. As noted above, the criteria could inter alia reflect earlier arrangements; bio-geophysical conditions; economic arrangements; or simply signify the comfort of a group of countries to work together.

It would also oversee the production of a strategic guidance document which would (inter alia) establish:

- An agreed division of the globe into regions:
- A fundamental sample/media matrix;
- Agreed sampling and analytical methodologies;
- Protocols for QA/QC;
- Protocols for compilation of regional assessments;
- A strategy for capacity building based upon the concept of a tiered capacity; and,
- Include a draft annotated generic table of contents for each regional assessment.

b) The convention secretariat would provide (or make arrangements for) coordination / management services to the global advisory group, including maintaining the website already launched by UNEP Chemicals.

c) The regions would be the operational units for data gathering, analysis, and assessment. A regional advisory group will in each region be responsible for translating the global strategic plan into a regional reality. Some important tasks for regional advisory group will include:

- Deciding upon its composition. It is suggested that it should have two forms of membership. A small core group, built around the key authors who will produce the regional assessment, and a larger group which will include all of the participating Parties. The latter group should meet at the time of programme initiation to provide initial direction, but would then communicate by telecommunication to monitor progress. The core group would organise and execute most of the work at the regional level relying heavily upon national contacts.
- Transform the global sampling and media matrix into a regional reality. For example, if the global plan calls for a biological medium to be selected that is a good upper food chain indicator of POPs biomagnification, the regional group will decide which species to select.
- Decide upon the number of participating laboratories within each region. This would take into account such issues as capacity, cost effectiveness, sustainablity, and the imperitive of maintaining data harmonization and data quality assurance and quality control.
- Regionally implement the globally agreed measures for QA/QC to ensure that:
  1) a regional assessment of temporal trends can be produced; and,

2) support a assessment of regional transport.

- Work with the Convention Secretariat to help develop a tiered approach for laboratory infrastructure, using existing facilities as much as possible but developing capacity when necessary.
- Work with National focal points to make arrangements for national contributions of data and (when appropriate) national analytical services;
- Work with international organizations to make arrangements for their participation as required.

d) The convention secretariat would provide (or make arrangements for) coordination/ management services to each regional advisory group.

e) National focal points would be established by each participating Party in order to arrange for the contribution of samples and possibly of analytical services.

f) As noted throughout this paper, the arrangements to evaluate effectiveness from the viewpoint of "regional and global transport" will be somewhat different from those associated with the detection of temporal trends. It is therefore suggested that as a priority, a small group of experts be asked to identify several optional practical products for this component of the assessment and to indicate the tools they would require to complete each option at both a regional and global level. Appropriate decisions on the matter would then be taken by the global advisory group.

g) The global advisory group (in consultation with the regional groups) would be responsible for making arrangements to consolidate results of the regional analyses into a global assessment of temporal trends and global transport. Both the consolidation and the regional reports would be made available to the COP for the purposes of effectiveness evaluation.

8) Final comment

The combined elements of Article 16 (environmental monitoring, national reporting, and compliance) are an innovative feature of the Stockholm Convention. They promise to equip the COP with the ability to detect whether the environment is benefiting from the collective actions agreed upon in the Convention, and to indicate possible strengths and deficiencies in those collective actions. Together with Articles 8 (Listing of Chemicals in Articles A, B, and C) and 19 (Conference of the Parties), they are essential to ensuring that the Convention is a living agreement that can evolve intelligently over time. It will be an exciting opportunity to participate in the design, implementation, and assessment phases of the environmental monitoring component. However, we must be under no illusion. It will be a challenging task. In the opinion of this author, if we are to achieve the opportunity presented to us, we will always seek simplicity at every stage.

**APPENDIX: FUNDAMENTAL CRITERIA FOR DESIGN AND
IMPLEMENTATION OF THE GLOBAL MONITORING AND ASSESSMENT OF
POPS IN RELATION TO THE NEEDS OF ARTICLE 16**

CRITERIA DRAWN FROM THE CONVENTION

- *The objective is to gather and assess information on POPs in the environment. It is not concerned with National Reports, with non-compliance, or with hot spot detection (Boundary Observation 1)*;
- *It is obligatory only to consider the substances contained in the Annexes*, but they need not all be measured in all elements of the sampling matrix *(Boundary Observation 3)*
- *The assessment of temporal trends (essential for effectiveness evaluation) could be given a regional focus, although this must have a global context in relation to environmental transport (Boundary Observation 4)*
- *The challenges of obtaining comparable monitoring data (inter alia harmonization, QA/QC) and of the world mosaic of capacity argue for identifying the absolute minimum data set necessary to inform the COP on trends (Boundary Observation 7).*
- *Non-parties may be encouraged to contribute acceptable information to the programme if they wish. However, countries participating in this way would be "passive", and unable to take part in decision making, or be members of the assessment writing teams. (Boundary Observation 8).*

CRITERIA DRAWN FROM OBSERVATIONS OF OTHER PROGRAMMES

Successful monitoring programmes strive for:

- *Inclusiveness and transparency in all aspects of the programme design, conduct, and in the assessment process*;

- *Clarity of: design for the sampling activities; of expectations for standards of analytical performance; and of arrangements for QA/QC;*

- *Simplicity in all aspects of monitoring and assessment activities*;

- *Long term sustainability of all arrangements and activities;*

- *Adopting regionalization frameworks that work best for the work to be performed, rather than necessarily adopting pre-existing arrangements;*

- *Plasticity, in order to ensure the ability to meet evolving demands of the Convention.*

- *Use a tiered approach to such elements as the sampling matrix in order to preserve basic simplicity while allowing the programme to explore new areas.*

- *A clear understanding of data ownership*;

- *Provide clear, uniform, and comprehensive guidance to all members of the assessment teams on the objectives of their task*;

- *Provide clear accountabilities for those involved in the assessment and include mechanisms to promote accountability;*

- *Include mechanisms to ensure unencumbered access to data for the assessment, including vital supportive information (e.g. age or sex of species from which samples may have been taken).*

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Substances and Analytical Techniques

Background Paper for the UNEP POP Workshop, 24-27 March, Geneva

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Abstract

The primary focus will be on the 12 POPs and it is suggested that about 20 individual organochlorine pesticides (OCPs) and 30 PCB congeners be determined. In addition, all 2,3,7,8-polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), as well as the 12 planar PCBs for which TEFs have been assigned, should be determined. To achieve concensus on a detailed list it may be necessary to categorize chemicals as Essential, Essential-sub-regional (ES) or Recommended depending on the analytical capacity and importance of the chemicals regionally. For ortho-PCBs and OCPs, no single, detailed, step by step, analytical method is recommended. Instead it is proposed that the process be "unified" using an interlaboratory calibration program. Use of a single method for the extraction, isolation and quantification steps for PCDD/Fs (along with non-ortho-PCBs) is recommended in order to be in compliance with ongoing programs.

In May 2001, the global community accepted the Stockholm Convention on Persistent Organic Pollutants (POPs) with an objective to protect human health and the environment. The Convention includes measures to reduce further emissions to the environment, for both intentionally and unintentionally produced POPs, and global monitoring is being planned to evaluate the effectiveness of the measures. The 12 substances, all of which are characterized as chlorinated hydrocarbons, that are currently listed in Annexes A, B and C of the Convention are the initial focus for global monitoring. The objectives for this working group are:

1. Describe how to set priorities for the substances in different regions
2. Recommend analytical techniques to be used in order to develop comparable data on environmental levels globally
3. Define the capacity necessary for implementation of our recommendations

1. Priorities for substances

The primary focus will be on the 12 POPs. These are: aldrin, chlordane, dieldrin, dichlorodiphenyltrichloroethane (DDT), endrin, heptachlor, hexachlorobenzene, mirex, toxaphene, polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins and – dibenzofurans (UNEP, 2001). Chemical structure, physical and chemical properties, source and use of these substances are listed in Appendix 1. It should be noted that these are "chemical substances" and not individual analytes that would be determined in practice. Most of the substances are all organochlorine pesticides (OCPs) that had been widely used because of long-term effect and cheap cost but abandoned their use in early 1970 in most of developed countries. Anticipated concentrations in environmental samples will in part be reflected by overall global production of the substances. The high production substances, such as PCB, DDT and toxaphene have exceeded more than on million tonnes in total (Appendix 2). The other OCPs are estimated between several ten thousand tonnes and 1 million tonnes. On the other hand, the production of PCDDs/PCDFs is very small, amounting several tonnes TEQ worldwide, which indicates that the detection of these substances in back ground area is difficult. In the following sections, the pros and cons of including various individual analytes are considered.

1.1. PCBs and OCPs

These can be considered together because they are extracted and analysed together in most cases as discussed in Section 2. In practice, most laboratories specializing in POPs analysis determine about 30 or more individual PCB congeners, and 10-20 individual OCPs and their metabolites, regardless of the sample matrix. A list of individual analytes recommended for the AMAP Program (AMAP 2000) is included in Appendix 2 as an example. Other ongoing POPs monitoring programs vary in their analyte lists. For e.g. Integrated Atmospheric Deposition Network (IADN) in the Great Lakes region of North America includes over 100 PCB congeners (IADN 2002) while the UNEP/World Bank/GEF project on Persistent Organic Pollutants, Food Security, and Indigenous Peoples in Arctic Russia included 15 PCB congeners (RAIPON/AMAP/GEF Project, 2001).

It may be difficult to achieve consensus on the detailed list. However some minimum numbers must be set in order to compare concentrations. For PCBs, the Arctic Monitoring and Assesment Program (AMAP) has used as a minimum the so-called "ICES 7" (International Council for Exploration of the Sea) of PCBs 28/31, 52, 101/90, 118, 138, 153 and 180, and this list is also used for routine monitoring of fish and food products around the world. Using only 7 congeners severely underestimates total PCB concentrations in some matrices – mainly in abiotic samples such as air and sediment. On the other hand these 7 are robustly determined having been the subject of numerous interlab comparisons (e.g. QUASIMEME 2002).

To achieve consensus, AMAP categorized the chemicals as Essential, Essential-sub-regional (ES) or Recommended. The ES category allowed some countries to opt out either

because the analyte was not of interest or because of analytical concerns. An example is dieldrin, and its isomer endrin, which can be difficult for some laboratories because they are destroyed in sulfuric acid treatments that are intended to remove lipids. Such a categorization scheme might be appropriate for the global monitoring guidelines.

Toxaphene is the most a problematic chemical in the list of OCPs. Current programs in Europe are determining three Parlar congeners (P26, P50 and P62) and interlaboratory comparisons have shown reasonable agreement for these congeners among laboratories (deBoer et al. 2000). However P26 is interfered with by co-eluting chlorobornanes in some matrices and P62 can vary widely in its instrumental response. Furthermore in North America, most datasets for toxaphene are still based on quantification with technical toxaphene which yields a single value and no congener specific information. Capacity for determining toxaphene outside of the USA, Canada and western Europe, is very limited judging from the relatively large amount of measurements from these countries and the dearth of measurements elsewhere. Toxaphene is probably an example of a Recommended or ES category chemical. On the other hand given prevailing high levels of toxaphene in some locations (e.g. biota in the Barents Sea, Great Lakes fish, North Atlantic and North Pacific marine biota), and its restricted by potential use in some countries (UNEP 2002) information from a wide range of countries and not just North America and Northern Europe, would be desirable.

Another consideration for setting priorities is whether there to use global use information inferred from the UNEP Masterlist of POPs use and regulatory action (UNEP 2002) to determine if only POPs should be determined in certain regions. However, given the relative ease of determining almost all pesticides on the POPs list, except toxaphene, as well as ortho-substituted PCBs this does not seem necessary.

1.2. PCDD/PCDFs and non-ortho PCBs (*no*-PCB)

This group needs to be considered separately because analytical methodology is normally quite different from that used for ortho-substituted PCBs and OCPs. Virtually all current measurements of PCDD/Fs use analyte isolation/enrichment schemes involving adsorption on carbon as well as other steps (e.g. sulfuric acid silica columns) that are not commonly used for other POPs. Furthermore GC-high resolution MS (EI mode; resolving power 10000) is the preferred method of quantitation (US EPA 1998). It has become routine to include *no*-PCBs (77, 81, 126 and 169) in the same analysis because they can be isolated by the same procedure (USEPA 1999). The GC-high resolution MS procedure has high precision and reproducibility because of the use of the isotope dilution method involving internal C13 standards for each PCCD/F homolog group. Ideally the analysis would also include the mono-ortho (*mo*) PCBs 105, 114, 118, 123, 156, 157, 167, as well as di-ortho PCB 170 (2,2',3,3',4,4',5-heptachlorobiphenyl) for which there are TEFs assigned by WHO. However, the latter 8 congeners can also be determined by GC-ECD as part of an expanded list.

Development of global information on PCDD/F is important because, in addition to their presence as byproducts in various chlorinated chemical products, these compounds are produced by low temperature burning which is significant problem especially in developing countries lacking the capacity for incineration or secure land filling of municipal wastes (Tanabe 2002). *No*-PCB and *mo*-PCBs should be included with PCDD/Fs because they have well established TEFs and therefore a total TCDD TEQ concentration can be determined. However, the high costs of PCDD/F and *no*-PCB analysis means that this group is not routinely included in most monitoring programs in North America and Europe (for example they are not part of IADN or AMAP) although they are quite routinely determined in Japanese monitoring programs (Morita 2002). It is therefore unlikely that this group can be recommended for routine monitoring globally unless a program is developed with funding to support analysis of samples from around the world, in one or a small number of labs.

Most labs currently determine only 2,3,7,8-substituted PCDD/Fs. While this is sufficient for assessment of human and wildlife exposure it is inadequate for source

identification. Thus some researchers interested in combustion sources of PCDD/Fs routinely determine non-2,3,7,8-substituted PCDD/Fs including di- and trichloro- substituted congeners. If PCDD/Fs were included in global program and air was being monitored then inclusion of non-2,3,7,8-substituted congeners would be recommended.

1.3 Other compounds

Additional candidate chemicals should satisfy the scientific criteria for POPs including persistence, bio-accumulation, potential for long range transport and adverse effects. An additional consideration is that these compounds be readily isolated with the same procedures as the 12 POPs so that no special sampling or analytical program would necessary to include them. In the flame retardant and byproduct category these would include the tetra – to octabromo-diphenyl ethers, hexabromocyclododecane, polychlorinated terphenyls (PCT), short chain chlorinated paraffins, octachlorostyrene and hexachlorobutadiene. Chlorinated naphthalenes can be isolated along with *no*-PCBs. Chlorinated insecticides endosulfan and methoxychlor and the DDT impurities tris(p-chlorophenyl) methane and -methanol are also candidates for this list. Many of these compounds are in the process of being proposed as candidates for addition to the POPs list in the future and therefore it would be useful to use the Global program to develop information on their occurrence in the environment. Possible, non-chlorinated candidates such as benzo(a)pyrene, tributyl tin and perfluorooctanesulfonic acid (PFOS) are not recommended to be included in this list because of the need for different extraction, isolation and detection steps in comparison with neutral chlorinated or brominated organics.

In summary, the decision is to be made in the selection of substances among the following choices:

(1) 12 POPs
(2) 12 POPs plus major isomers, metabolites and impurities
(3) 12 POPs minus specific substances that may not be important
(4) 12 POPs plus major metabolites and impurities minus specific substances
(5) 12 POPs plus candidate new POPs
(6)   12 POPs plus major isomers, metabolites and impurities plus candidate new POPs

2. Recommended analytical techniques

In this section we will consider analytical techniques to be applied in order to quantitatively determine concentrations of the individual analytes in environmental samples. The type of samples, collection methods, ancillary data needed for interpretation of the results, storage conditions and so on, are covered by other working groups. Our task is to develop guidance for the laboratory phase of monitoring program.

UNEP will eventually have to have a strategy in place for deciding how many laboratories will participating in the global POPs monitoring. The amount of guidance needed for analytical methods will of course depend on whether this strategy includes developing new laboratories, and/or training programs for lab personnel, in certain regions which have relatively few facilities and little experience in international programs, e.g. Africa, or whether one or more existing labs on each continent or region would be selected. For discussion purposes we will assume that well equipped labs headed by analytical chemists with some experience in analysis of POPs will be selected for the program. These labs and individuals will already have analytical methods running for some matrices but may need guidance for others.

Analytical methods for the determination of POPs in environmental samples and biological tissues vary depending upon the matrix and required limit of detection. Analytical procedures are composed of the following four steps: 1) sample collection and extraction, 2) clean-up using partition and chromatographic fractionation 3) separation on gas chromatography (GC), 4) detection with selective and sensitive detectors. Since the 1960s,

POPs have been determined using gas chromatography (GC) techniques with electron capture detection (ECD), initially using packed columns. More advanced methods, such as capillary GC-ECD and GC coupled with mass-spectrometry (GC-MS) have been used in recent studies to identify the individual congeners, to improve the comparability of the analytical data from different sources and to establish a basis for the understanding of geochemical cycles and toxicological implications.

2.1. Extraction and isolation of PCBs and OCPs

Numerous methods have been published over the past 30 years on the specific analytical techniques for determination of PCBs and OCPs in food and environmental matrices. Laboratory standard operating procedures for analysis of POPs are available from agencies such as US EPA, NOAA (Status and Trends Program 1998), ICES (Techniques in Marine Environmental Sciences; www.ices.dk/env), OSPAR (Joint Assessment and Monitoring Program; www.ospar.org), International organization for Standardization (http://www.iso.org), Association of Official Analytical Chemists International (http://www.aoac.org/), Japan Environment Agency and Gosstandard of the Russian Federation. Not all of these sources provide analytical SOPs for all environmental media. A useful activity for the Global POPs Monitoring program would be to prepare a list of agencies and the addresses and titles of the recommended laboratory SOPs.

Given the broad range of technical expertise for analysis of PCBs and OCPs, as evident from large international participation in interlab calibration projects for these compounds that have been run by QUASIMEME (http://www.quasimeme.marlab.ac.uk/), no single, detailed, step by step, analytical method can be recommended. Instead it is proposed that the process be "unified" using an interlaboratory calibration program run by an experienced organization such as QUASIMEME. The details on the QA program would be defined by the QA Working Group. Thus participants would be free to use their own methods for a given environmental matrix, although guidance would be provided as to best laboratory practices (See Table 1), and participation would be mandatory for labs identified as being in the global program.

In addition to developing an interlaboratory program, UNEP could also assure good interlaboratory agreement by circulating a set of certified analytical standards for the POPs of interest. Certified reference materials encompassing major environmental matrices such as fish oil, whale blubber, soil and sediment would also be recommended e.g. NIST or BCR.

Table 1 provides general guidance for various preparation, extraction and isolation steps in the analysis of PCBs and OCPs and sources of information. Starting with sample preparation, the basic approach is to assure that the sample is prepared for extraction in a room that is free of significant contamination. Ideally this would involve a well ventilated lab with air prefiltered through HEPA and carbon filters but any clean chemical laboratory facility should be adequate for most work on PCBs and OCPs in most matrices except water, or soils and sediments from remote locations.

Wet samples should not be air-dried to avoid contamination from lab air, especially in the case of PCBs (Wallace et al. 1996), and to avoid possible volatilization losses. Instead homogenized samples should be mixed with a drying agent such as sodium sulfate or Celite. The drying agent must be certified to be free of POPs e.g. by heating at high temperature in the case of sodium sulfate or pre-extraction (Celite).

A standard QA step in the lab is to include a surrogate recovery standards in each sample. Generally one or two PCB congeners (e.g. CB30 and CB204) and OCPs e.g. pentachloronitrobenzene. If GC-MS is being used as the detection system then ^{13}C-labelled surrogates can be used .

The appropriately prepared sample can then be extracted by any one 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 (sample in a glass thimble) or semi-automated systems (e.g. pressurized fluid

extractors). 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 a major consideration here. Only high purity glass distilled solvents should be used.

Table 1. Guidance for various preparation, extraction and isolation steps in the analysis of PCBs and OCPs

Environmental Matrix	Analytical steps	General procedures
Soil and sediment	Preparation	Prepare in a PCB and pesticide free room Avoid air drying. Wet sieve if necessary to remove large objects. Centrifuge sediment to remove excess water. Mix soils/sediments with drying agent. Separate determination of dry mass by oven drying. For sediments total organic carbon should be determined.
	QA	One blanks, soil CRM very 10 samples; spike all samples with recovery surrogate standards. Bake glassware by overnight heating at 200°C or higher.
	Extraction	Soxhlet, Pressurized Fluid Extraction, or reflux - with acetone: hexane or DCM Solvent evaporation – transfer to hexane. Sulfur removal with (acid) activated copper particles may be required for sediment
	Isolation/cleanup	Silica or Florisil elutions – non-polar (hexane) and polar (DCM: hexane or equivalent) fractions
Plants	Preparation	Homogenize using food chopper or blender. Cryo blending is useful. Mix with drying agent. Separate determination of dry mass by oven drying.
	QA	Same as soil. Use plant CRM if possible
	Extraction	Same as soil.
	Isolation/cleanup	Same as soil.
Fish and shell fish	Preparation	Select muscle or liver depending on species. For mussels and crustaceans use soft tissue. Select tissue that has not been in contact with the sample container. Homogenize using food chopper or blender. Cryo blending is useful Mix with drying agent. Separate determination of lipid content - recommended method to be discussed.
	QA	Same as soil. Use fish or mussel SRMs
	Extraction	Soxhlet, Accelerated Solvent Extraction, or column extraction Use acetone: hexane or DCM
	Isolation/cleanup	Remove lipid using gel permeation chromatography if possible or by repeated washing of the extract with sulfuric acid. Follow with fractionation on Silica or Florisil columns as described for soil
Marine mammal blubber	Preparation	Select blubber that has not been in contact with the sample container. Blend or hand mix with drying agent. Separate determination of lipid content - recommended method to be discussed.
	QA	Same as soil. Use fish oil or marine mammal SRMs
	Isolation/cleanup	Same as for fish extracts

Air (high volume)	Extraction,QA and cleanup	Assuming that air is collected on polyurethane foams or XAD resin these would be extracted in a Soxhlet or Pressurized fluid extractor. Other steps as for soil or sediments
Semi-permeable membrane devices (SPMD)	Preparation	SPMDs would be removed from their transport cases and rinsed with precleaned water to remove accumulated dust (air borne samplers) or periphyton (water samplers)
	Extraction,QA and cleanup	Assuming that the SPMD is lipid based, extraction of POPs by "dialysis" into hexane would be achieved in a large glass cylinder
Human blood		To be added if required

Isolation steps can be relatively straightforward for low lipid samples such as soils, sediments and vegetation. 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 PCBs (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. p,p'-DDT.

For high lipid samples, such as fish tissue and marine mammal blubber, a lipid removal step must be included. This can be achieved using size exclusion or gel permeation chromatography (GPC) either in automated systems, using 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 GC vials for analysis. Addition of an internal 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.

Determination of PCBs and OCPs in air, surface or ground water samples, snow or precipitation, presents a special situation in terms QA and blanks. There are fewer labs specializing in the sampling and analysis of POPs in air and water and the analysis is more demanding because of much lower concentrations than in soils, sediments and biotic samples. Sampling under conditions which avoid contamination presents a major challenge especially for PCBs. Sampling techniques for water are discussed by the Working Group on Site Selection/Matrices Selection and Sampling. Sampling of air and water has to be closely coordinated with the lab because of the need to prepare clean samplers e.g. solid phase cartridges or semi-permeable membrane devices (SPMD) cartridges prior to their deployment. Clean facilities, ideally with HEPA and carbon filtered air are recommended. Assuming that the QA and blank concerns have been dealt with then water sampling devices, e.g. solid phase cartridges or SPMDs are extracted by elution and dialysis, respectively. The elution of reverse-phase or XAD resin water sampler cartridges generally involves use of a water miscible solvent first to remove water followed by a solvent of intermediate polarity such as DCM. Combined extracts are then partitioned into hexane. Particulate phases collected by filtration on glass fiber filters are treated like sediments and extracted by Soxhlet or pressurized fluid extraction.

Air sampling for POPs will be addressed by the Working Group on Site Selection/Matrices Selection and Sampling. Assuming that polyurethane foam (PUF) or XAD resin are used, as the most common absorbants in high vol samples, then extraction would proceed by elution of the cartridge using Soxhlet or pressurized fluid extraction. Lipid based SPMDs passive air samplers would be cleaned to remove dust on the outside of the plastic tubing and then dialysed with hexane.

2.2. Extraction and isolation of PCDD/Fs and *no*-PCBs
2.2.1. Conventional extraction/GC-MS analysis
Analytical methodology for PCDD/Fs and *no*-PCBs differs from those used for routine ortho-PCBs and OCPs in requiring much lower detection limits (typically 10-100 times lower) because guideline limits for levels in food products are in the low ng/kg range and Tolerable daily intakes are in the 1-4 ng TCDD TEQs/kg body weight per day range. To achieve these detection limits methodology for PCDD/Fs uses isotope dilution MS (^{13}C-surrogates for all PCDD/F homolog groups), enrichment on carbon to isolate planar compounds, very small final volumes (10-50 uL) for GC analysis and GC-high resolution mass spectrometry for quantitation. Methodology for PCDD/Fs, slightly modified to include *no*-PCBs, developed by the US EPA (1998;1999) is well established and validated by numerous interlab comparisons. This methodology would be recommended for use in a global monitoring program. Unlike the guidelines for PCBs and OCPs, this very specific guidance for the extraction, isolation and quantification steps for PCDD/Fs is recommended in order to be in compliance with ongoing programs and compatible with results generated with these methods over the past 10 years.

2.2.1. Bioassay screening
If PCDD/Fs are considered an important issue a second approach would be to screen extracts using a bioassay technique. Rapid, sensitive and inexpensive screening tools, such as in vitro cell bioassays, are available to screen environmental and biological samples for the presence of dioxin-like compounds (PCDDs/Fs and *no*-PCBs). If PCDD/Fs are considered an important issue, a second approach would be to screen sample extracts using a bioassay technique. Rat hepatoma H4IIE cell bioassay is one of the commonly used techniques in several laboratories (Hilscherova et al., 2000). The in vitro bioassays involve culturing of cells in the laboratory, seeding the cells in 96-well plates, dosing the sample extracts onto cells, incubation for 24-72 h, and measurement of EROD activity or luminescence activity, depending on the cell types. The assays are relatively fast and inexpensive and are good screening tools. If activity is detected, then instrumental analysis could be performed. The bioassay technology could be relatively easily transferred to many laboratories which would otherwise not be capable of PCDD/F determinations.

2.3. GC analysis
Numerous analytical approaches are available for quantifying PCBs, and OCPs, as well as PCDD/Fs by gas chromatography. As with extraction/isolation steps only general guidance is required for ortho-substituted PCBs and OCPs. However, a major consideration is that the laboratories will have access to modern capillary GC equipment and either electron capture or mass spectrometry detection. Some general guidance on the application of gas chromatographic analysis of ortho-substituted PCBs and OCPs is provided in Table 2. For PCDD/Fs and no-PCBs, quantification solely by isotope dilution high resolution mass spectrometry is recommended and details can be found in SOPs (e.g. EPA method 8290A). HRMS can also be used, of course, for determination of all ortho-substituted PCBs (e.g. EPA Method 1668) and OCPs as well 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 ortho-PCBs and OCPs at low ng/g levels or higher in environmental matrices.

Table 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-subsituted PCBs & all OCPs on the POPs list except toxaphene	30 or 60 m x 0.25 mm id. Column with H2 carrier gas. Dual column non-polar (DB-1) and intermediate polarity columns (DB-5)	Relatively inexpensive and easy to operate. Similar response factors for most OCs Good sensitivity for all POPs. Adequate for routine tasks. High potential for mis-identification 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 PCBs & 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 for target POPs	Moderately expensive and more complex to operate and maintain. Newer instruments (post 1997) have adequate sensitivity for routine POPs monitoring at low pg/uL 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 tech mixture)
Quadrupole Mass spectrometry in Electron capture negative ionization (ECNIMS) mode.	Toxaphene and other highly chlorinated OCPs and PCB with > 4 Chlorines	30 m x 0.25 mm i.d. low bleed columns with He carrier gas. Selected ion mode for target POPs	Comparable sensitivity to ECD in SIM mode for some POPs, in ECNIMS mode. Much less potential for mis-identification than with ECD	Examples: DDT/DDE ~ 0.1 pg HCB ~0.1 pg Dieldrin ~ 1 pg Toxaphene ~ 10 pg (as tech mixture)
Ion trap mass spectrometry using MS/MS mode	All PCBs, 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 tech mixture)
High resolution magnetic sector Mass spectrometry in Electron ionization (EI) mode	PCDD/Fs, all PCBs, 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 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 tech mixture)

[1]Instrumental detection limits at S/N of ~10.

2.4. Recommended Detection limits

The choice of what detection limits to set for POPs in the Global monitoring program will be an interesting challenge for the UNEP workshop. This issue is one shared by three working groups. Detection limits depend, of course, on the analytical method but also on the sample size and QA considerations e.g. information available from blank or control samples and recovery studies.

The selection of detection limits also depends on the goals of program and how much emphasis is placed on reliability of the results versus need to achieve broad geographic coverage and avoid reporting "less thans" for a high proportion of samples.

First, some definitions: Method detection limit (MDL) is defined as according to Keith (1991a) as = blank +3*SD of the blank where the multiplier 3 is approximately the t value (t0.01,n-1) for N>7 (USEPA 1984). If the blank is zero then lowest concentration that the instrument can detect+3*SD of low concentration analysis (replicated at least 7 times) is used. These detection limits are usually expressed as a concentration i.e. based on the average weight of sample analysed.

The MDL has also been defined using 2*SD depending on the needs of the data user (Keith 1991b). MDL3SD represents the background concentration that would be greater than 99% of the method blanks (or >99% of the IDL if the blank = nondetect). MDL2SD represents the background concentration that would be >95% of the method blanks (i.e., the error rate of false positive is 5%). Even larger degrees of confidence can be built into the MDL by using a large error term. Thus for 6*SD above the mean blank [the Reliable Detection Limit (Keith 1991b)] the error rate of false positives is 0.1%. The risk of false positives becomes lower as one uses the higher value. MDL2SD was recommended for use in a study of blank levels of co-planar PCB congeners by the USEPA (Ferrario et al., 1997).

While most labs will be able to achieve very similar limits for instrumental detection, i.e. assuming they are using analytical standards and similar instruments (ECD or various MS systems) for individual PCB congeners and OCPs, MDLs will vary among labs due to blank considerations, choice of multiplier, sample size as well as final volume and volume injected into the instrument.

Table 3 presents some tentative guidelines for MDLs that should be achievable assuming low blanks for the individual PCBs and OCPs in a 10 gram sample.

Table 3. Estimated method detection limits for individual PCBs and OCPs (ng/g) assuming 10 g sample and sample volume of 0.5 mL

Analyte	ECD	MS (low resolution; SIM)	MS (high resolution; SIM)
PCB 28	0.05	0.1	0.01
PCB 52	0.05	0.1	0.01
PCB153	0.05	0.05	0.005
PCB180	0.02	0.02	0.005
P,p'DDE	0.05	0.05	0.01
a-HCH	0.01	0.04	0.01
HCB	0.01	0.02	0.005
Cis-chlordane	0.03	0.05	0.01

Assumes MDL = blank or lowest instrument response + 2*SD

Lower detection limits could of course be achieved for ortho PCBs and OCPs by using isotope dilution high resolution MS with small final sample volumes as is done for PCDD/Fs and *no*-PCBs. However, this would be difficult to implement in some regions of the world because of the expense of purchasing and operating high resolution instrumentation. Furthermore since

the vast majority of results from most current international monitoring programs for ortho-PCBs and OCPs have used GC-ECD or GC-low resolution MS analysis, use of HRMS does not seem worth the effort. Nevertheless, close attention should be paid to the detection limit issue in planning the monitoring program so that the amount of usable data, i.e. >MDL, is maximized.

2.5. Data reporting
This aspect overlaps with the interests of the Working group on QA/QC and data treatment. The objective here would be to have a record of the entire processing of the sample from preparation through to reporting concentrations that can be evaluated independently. Therefore the individual labs should report concentrations for analytes, blanks and reference materials. Data reports should also include instrument calibration results. This would enable MDLs to be calculated independently of the lab if necessary. A procedure similar to that used by QUASIMEME for collecting interlab study data should be used. Concentrations should be reported on a dry weight basis for soils, sediments and vegetation. Lipid content should be reported for biota samples although concentrations should be reported on a wet weight basis.

Conclusions and recommendations

1. A list of individual PCB congeners (at least 30) and OCPs and metabolites (at least 20) should be selected. At a minimum the "ICES 7" PCBs should be used.
2. Recommendations for individual compounds could be regionally based i.e. by a rating system like that of AMAP's.
3. Toxaphene should be included but may have to be in the "recommended" rather than "essential category" due to analytical considerations
4. For ortho-PCBs and OCPs, no single, detailed, step by step, analytical method is recommended. Instead it is proposed that the process be "unified" using an interlaboratory calibration program run by an experienced organization such as QUASIMEME
5. A useful activity for the Global POPs Monitoring program would be to prepare a list of agencies and the addresses and titles of the recommended laboratory SOPs for POPs analysis.
6. A specific method (EPA 1613 and 8290A) for the extraction, isolation and quantification steps for PCDD/Fs (along with *no*-PCBs) is recommended in order to be in compliance with ongoing programs and compatible with results generated with these methods over the past 10 years.
7. Close attention should be paid to the detection limit issue in planning the monitoring program so that the amount of usable data, i.e. >MDL, is maximized.
8. The amount of guidance needed for analytical methods will depend on whether UNEP POPs monitoring strategy includes developing new laboratories, and/or training programs for lab personnel, in certain regions which have relatively few facilities.

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2734

Appendix 1. Physical-chemical properties of selected individual components of POPs substances

Common name	Isomer/congener/abbreviation or chemical name	Formula	CASN	Molecular weight	Water solubility[1], (mmol/m^3) (at 25°C)	Log Kow (at 25°C)	Henry's Law Constant, H (Pa m^3/mol) (at 25°C)	Vapor pressure[2], Pa (at 25°C)	Atmospheric half-life (hrs)	References
Organochlorine pesticides										
Aldrin	Aldrin	$C_{12}H_8Cl_6$	309-00-2	364.9	0.0465	6.5	4.46	0.0160	6.1	1,2
Chlordane	cis-CHL	$C_{10}H_6Cl_8$	5103-71-9	409.8	0.137	6.0	0.342	0.0004	55	1
	trans-CHL	$C_{10}H_6Cl_8$	5103-74-2	409.8	0.137	6.0	0.262	0.00052	55	1
DDT	o,p'-DDE	$C_{14}H_8Cl_4$	3424-82-6	318	0.126	5.8	7.95	0.000866	170	1
	o,p'-DDT	$C_{14}H_9Cl_5$	789-02-6	354.5	0.0733	6.0	0.347	2.53×10^{-5}	115	1
	p,p'-DDT	$C_{14}H_9Cl_5$	50-29-3	354.5	0.0155	6.2	2.36	2.0×10^{-5}	170	1
Dieldrin	dieldrin	$C_{12}H_8Cl_6O$	60-57-1	380.9	0.446	5.2	1.12	0.0005	55	1,2
Endrin	Endrin	$C_{12}H_8Cl_6O$	72-20-8	380.9	0.6563	5.2	0.64	0.0004	43	1,2
Heptachlor	Heptachlor	$C_{10}H_5Cl_7$	76-44-8	373.3	0.482	6.1	29.8	0.053	6.5	1,2
Mirex	mirex	$C_{10}Cl_{12}$	2385-85-5	545.5	0.000119	6.9	839.4	0.0001	170	1
Toxaphene	technical	$C_{10}H_{10}Cl_8$	8001-35-2	413.8	1.21	5.5	0.745	0.0009	170	1
	P26	$C_{10}H_{10}Cl_8$	-	414	-	5.5	-	-	-	3
	P50	$C_{10}H_9Cl_9$	-	448	-	5.8	-	-	-	3
Byproducts & industrial chemicals										
Hexachlorobenzene	HCB	C_6Cl_6	118-74-1	284.8	0.0176	5.5	131	0.0023	17000	4
Polychlorinated dibenzo-p-dioxins	TCDD	$C_{12}H_4O_2Cl_4$	30756-58-8, 67028-18-6, 30746-58-8, 1746-01-6	322	0.000993-0.0013	6.60-7.10	0.704-3.747	2.00×10^{-7}-1.00×10^{-6}	170	5
	PnCDD	$C_{12}H_3O_2Cl_5$	39227-61-7	356.4	0.000331	7.4	0.266	8.80×10^{-8}	550	5
	HxCDD	$C_{12}H_2O_2Cl_6$	39227-26-8	391.0	1.13×10^{-5}	7.8	1.084	5.10×10^{-9}	550	5
	HpCDD	$C_{12}HO_2Cl_7$	35822-46-9	425.3	5.64×10^{-6}	8.0	1.273	7.50×10^{-10}	550	5

Group	Compound	Formula	CAS	MW	Water sol[1]	log Kow		Vapour pressure[2]		Ref[3]
	OCDD	$C_{12}O_2Cl_8$	3268-87-9	460	1.61×10^{-7}	8.2	0.684	1.10×10^{-10}	550	5
Polychlorinated dibenzofurans	TCDF	$C_{12}H_4OCl_4$	51207-31-9	306	1.37×10^{-3}	6.1	1.461	2.00×10^{-6}	170	5
	PnCDF	$C_{12}H_3OCl_5$	57117-31-4	340.42	6.93×10^{-4}	6.5	0.505	3.50×10^{-7}	550	5
	HxCDF	$C_{12}H_2OCl_6$	70658-26-9, 57117-44-9	374.87	2.2×10^{-5} - 4.72×10^{-5}	7.0	0.741-1.454	3.20×10^{-8} - 3.50×10^{-8}	-	5
	HpCDF	$C_{12}HOCl_7$	67462-39-4, 55673-89-7	409.31	3.30×10^{-6}	7.4	1.425	4.70×10^{-9} - 6.20×10^{-9}	550	5
	OCDF	$C_{12}OCl_8$	39001-02-0	443.76	2.61×10^{-6}	8.0	0.191	5.0×10^{-10}	550	5
Polychlorinated biphenyls	dichlorobiphenyls	$C_{12}H_8Cl_2$	25512-42-9	223.1	0.269-8.96	4.9-5.30	17.0-92.21	0.0048-0.279	170	3
	trichlorobiphenyls	$C_{12}H_7Cl_3$	25323-68-6	257.5	0.0582-1.55	5.5-5.90	24.29-92.21	0.0136-0.143	550	3
	tetrachlorobiphenyls	$C_{12}H_6Cl_4$	26914-33-0	292	0.0147-0.342	5.6-6.50	1.72-47.59	5.9×10^{-5} - 0.0054	1700	3
	pentachlorobiphenyls	$C_{12}H_5Cl_5$	25429-29-2	326.4	0.0123-0.0613	6.2-6.50	24.8-151.4	0.0003-0.0093	1700	3
	hexachlorobiphenyls	$C_{12}H_4Cl_6$	26601-64-9	360.9	0.0011-0.002	6.7-7.30	11.9-818	2.0×10^{-5} - 0.0015	5500	3
	heptachlorobiphenyls	$C_{12}H_3Cl_7$	28655-71-2	395.3	0.00114-0.0051	6.7-7.0	5.4	2.73×10^{-5}	5500	3
	octachlorobiphenyls	$C_{12}H_2Cl_8$	31472-83-0	429.8	0.00047-0.0007	7.1	38.08	2.66×10^{-5}	17000	3
	nonachlorobiphenyls	$C_{12}HCl_9$	53742-07-7	464.2	3.8×10^{-5} - 2.4×10^{-4}	7.2-8.16	-	-	17000	3

[1] water solubility of the chemical in the solid state;
[2] vapour pressure of the pure chemical in the solid state.
[3] References: 1. Mackay et al., 1997; 2. SRC database website: http://exc.syrres.com/interkow/physdemo.htm; 3. Fisk et al., 1999; 4. Mackay et al., 1991; 5. Mackay et al., 1992.

Appendix 2. Estimated global production of selected POPs

Chemical	Use	Production period	Est. total global usage / prod. (kt)[1]	Current annual emissions (kt)[2]	Reference
Legacy organochlorine pesticides					
DDT	Insecticide	1950-present	2600	-	Voldner and Li, 1995
Toxaphene	Insecticide	1950-1993	1330	-	Voldner and Li, 1995
Chlordane	Insecticide	1945-1988	78	-	Barrie *et al.*, 1992
Aldrin	Insecticide	1950-1992	500	-	Barrie *et al.*, 1992
Dieldrin	Insecticide	1950-1992	34	-	Barrie *et al.*, 1992
Legacy industrial organochlorines and by-products					
PCBs	Miscellaneous	1930-1992	1320	-	Breivik *et al.*, 2002
CB 28			57	-	Breivik *et al.*, 2002
CB 52			38	-	Breivik *et al.*, 2002
CB 101			31	-	Breivik *et al.*, 2002
CB 138			25	-	Breivik *et al.*, 2002
CB 153			27	-	Breivik *et al.*, 2002
CB 180			14	-	Breivik *et al.*, 2002
PCDD/Fs (as ITEQs)	By-products	1920-present	-	800-3.6×10^{-5}	UNEP, 1999
HCB	Pesticide by-product	1920-present	-	0.012-0.092	Bailey, 2001

Appendix 3. AMAP POPs analyte list. Adapted from Table B.2. AMAP Trends and Effects Programme, Section B, Trend Monitoring Programme (AMAP 2000).

Group	Individual Components	AMAP Programme status	Notes
Chlorobenzenes	HCB	Essential	
	Pentachlorobenzene	Recommended	not presently on the POPs list
	1,2,4,5-and 1,2,3,4-Tetrachlorobenzene	Recommended	2 –isomers not presently on the POPs list
Hexachlorocyclohex anes (HCH)	α-, β and γ-HCH	Recommended	3-isomers - not presently on the POPs list
Chlordane (CHL)	Cis- and trans-CHL	Essential	Other octa- and nonachloro- isomers may be present
	Cis- and trans-nonachlor	Essential	
	oxychlordane	Essential	Key metabolite
	MC4, MC5, MC6	Recommended	Important components
Heptachlor	Heptachlor	Essential	
	Heptachlor epoxide	Essential	Key metabolite
DDT	4,4'-DDE, -DDD, -DDT	Essential	DDE is important metabolite
	2,4'-DDE, -DDD, -DDT	Recommended	
Mirex	Mirex	Essential	
	Photomirex	Recommended	Important degradation product
Toxaphene	"total" toxaphene	Essential	Uses technical toxaphene as a standard
	Congeners P26, P50, P62	Recommended	
Dieldrin	dieldrin	Essential - subregional	
Endrin	endrin	Essential - subregional	
Aldrin	aldrin	Recommended	
PCB congeners (ΣPCB_7)	28/31, 52, 101/90, 118, 138, 153 and 180	Essential	
PCB congeners (ΣPCB_{30})	8/5, 18,28,31,44,49,52,95/66,87,99,101, 105/132,110,118,128,146,149,	Recommended	

	151,153,138/163,156,183,187,201/ 157,170,180,194, 195, 206,209	
Non-ortho PCBs	CB77, 126 and 169	Recommended
PCDD/PCDF	2,3,7,8-substituted tetra- to octachloro dibenzo-p-dioxins and dibenzofurans	Recommended

Sample Matrices, Site Selection and Sampling Techniques

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Abstract
In this briefing paper, we raise some general discussion points concerning the overall objectives of the monitoring programme. Matrix selection is considered in some detail. The merits/limitations of the following media are presented: active and passive air sampling; vegetation, soil, water, sediments, wildlife (e.g. bird eggs; marine mammals), human foodstuffs (milk/butter, eggs), human tissues (blood; milk). Related issues of sampling frequency, handling, storage, archiving etc., are also considered. Some suggestions are made for the programme design, to stimulate discussion at the workshop.

Introduction
The Stockholm Convention on POPs and other international agreements state that monitoring activities should be established to verify the effective implementation of the conventions and the subsequent improvements in environmental emissions and exposure. National monitoring activities are already in place in many countries, but not in others. There is a 'bias' as to the regions of the world where extensive monitoring is being undertaken. Monitoring programmes differ in their objectives and financial support, sophistication, approaches and methodologies etc. It is therefore difficult to compare rates of change and trends in different parts of the world.

The purpose of this paper is to provide a briefing document to direct discussion of the principles and strategies for *site and matrix selection*. In other words, it addresses the question: 'How should we sample regionally and globally, to assess the effectiveness of the Stockholm Convention?

Brief consideration of the objectives and some general issues
A number of broad discussion points need consideration. It is appropriate that these are considered, to help 'frame the scope' of the monitoring programme(s). The answers to these questions have an important impact on the more specific issues of sample matrix choice, numbers, frequency, analytes etc.

Generic issues include:
What are the requirements for monitoring under the Convention?
- It is appropriate to initially consider the required/intended scope of the monitoring programmes. Pertinent discussion points are:
- Is the requirement to show *source reduction*? If so, does this require attention on sources to the air, to water bodies, to soils, to food chains?
- Is the requirement to show *exposure reduction*? If so, does this require attention on humans (through the monitoring of food or the population) and susceptible biota (e.g. aquatic and terrestrial top predators?)
- Is the requirement to show *effects reduction*? If so, how could this be achieved in a monitoring programme?

- Are there cost-effective strategies, which can provide meaningful information, without requiring elaborate, multi-country, multi-media and highly time resolved data?

What are the possible monitoring strategies that could be adopted?
Under this heading, it is appropriate to consider:
- What are the roles and responsibilities of UNEP, and national/regional parties?
- Is UNEP intending to produce *specific recommendations* or a (lower) *level of guidance* on the requirements, design and implementation a monitoring programme?
- How will the resources required to undertake a monitoring programme be made available (i.e. internationally, regionally, nationally?).
- Will UNEP have a role in *co-ordination*?
- Can different levels of cost-effective monitoring be devised? For example, can regional 'super-stations' be developed, coupled to lower intensity monitoring at other locations?

What is the required optimum spatial scale for monitoring?
This heading focuses attention on questions such as:
- What do we mean by 'regional' and 'global' monitoring?
- Is it necessary for all signatory countries to provide monitoring data, or is regional information adequate?
- How much variability might there be in trends from one location to another, and what are the implications for the number of sites, sample type and frequency?

What are the issues to do with time for the monitoring programme?
- When we monitor to ensure downward trends are being achieved, what timescales are envisaged (months – years – decades)?
- Will different sampling media decline at similar rates, in response to a reduction in use/emission?
- How quickly do we expect levels of POPs to decline in a given medium, and what are the implications for sample frequency and analytical precision?
- Should sampling be concurrent at different locations regionally/globally, and for different media?
- If so, how should seasonality and other factors influencing the 'noise' of data be addressed?

Which chemicals should be included?
There is an initial list of 12 POPs, which have already been targeted by international signatories to the protocols. Some points for consideration are:
- Are the signatory countries required to undertake monitoring for all 12 compounds, to meet their obligations *or* could broader regional trends be monitored more cost-effectively instead?
- Can techniques and approaches be developed which are sufficiently flexible to allow any future additions of compounds to the priority list to be included subsequently?
- Does knowledge of their sources/properties suggest what sampling approaches are useful? For example, are the chemicals mainly emitted to air or water or

applied directly to soil? Once entering the environment in a specific matrix/form, are they mobile? Should monitoring therefore be focussed on source locations and/or the 'general' or background environment?

Matrix selection

This section considers the advantages and disadvantages of different sample matrices. This includes some comments on the information obtained by sampling a certain medium, and some practical issues of doing so.

Air

POPs are subject to long-range atmospheric transport (LRAT). Indeed, this is one of the main criteria governing their international control. POPs are supplied to terrestrial and aquatic systems via emissions to air, LRAT and deposition. Hence, it is considered that air is a <u>key medium</u> to be sampled under the global monitoring programme. A number of national/regional POPs air monitoring programmes are in existence (e.g. IADN in Canada/US; EMEP). These provide invaluable data on underlying trends in air concentrations.

Ambient concentrations of POPs fluctuate widely in space and time. An important challenge is therefore to consider how to address this variability in the sampling. Because POPs compounds encompass a wide range of vapour pressures, gas-particle partitioning behaviours and concentrations (e.g. PAHs can be ug-ng/m^3; PCDD/Fs, pg-fg/m^3), there are substantial difficulties in designing a multi-purpose sampling strategy and some compromises over sample time/volumes are almost inevitable. However, such issues can be addressed by short-term sampling/bulking etc.

<u>Active air sampling</u> The techniques for air sampling of POPs are well established. Typically, high volume (Hi-Vol) air samplers are used, with a head adapted to sample POPs from the particulate and gas phases (with a filter and sorbent trap, respectively). The air volume sampled before breakthrough occurs varies for different POPs and with temperature. Such 'active' air sampling requires a power supply, trained operators, dedicated sites and the financial resources to buy the Hi-Vol samplers. Careful consideration also needs to be given to the use of field blanks, pre-cleaning and preparation of the sampling media. However, detailed knowledge of the performance and requirements for such sampling exists, so that protocols can be developed. Active air samplers are most usefully installed at meteorological stations, where supporting information of temperature, wind directions, precipitation etc. are obtained to support data interpretation.

Active air sampling at a number of stations regionally/globally will be essential to the UNEP programme. Much can be learnt from existing networks, and some co-ordination/overlapping with existing networks may be possible.

<u>Passive air sampling.</u> Such techniques provide a cheap and powerful tool for obtaining detailed spatially resolved and time trend data relatively cheaply and efficiently. A number of exciting developments have been made in this field in recent years; the utility of passive samplers has been demonstrated for local, national and regional scale monitoring.

The general concepts behind passive air sampling have been discussed elsewhere (Ockenden *et al.*, 2001). A sorbent/solid phase sampler is used, to which gas phase POPs can partition (ad-/absorb). The mass of chemical on the sampler will increase with exposure time (kinetic uptake phase), and approach equilibrium. The time to equilibrium will vary, depending on the 'capacity' of the sampler. The rate of supply may be influenced by wind speed, deployment conditions and compound.

The advantages/opportunities of passive air samplers are as follows:
- Low cost
- Excellent opportunities for high spatial and temporal sampling resolution data
- No power supply needed, easy deployment and little operator training required

Their disadvantages/constraints are:
- Current techniques are still 'semi-quantitative', requiring knowledge of the sampling rate (m^3 air sampled/day) and the effects of temperature
- Optimisation of sampling requires further study, of the effects of wind speed, temperature
- Sampling is efficient for the gas phase component, but generally poorer for the particulate phase
- The time to reach gas phase-sampler equilibrium varies widely between POPs

The development of passive air samplers for POPs is an active area of research. Different designs are being tested/used. There is no consensus yet as to what is the 'best design'; indeed, it is probable that different samplers will be useful for different purposes (i.e. different time scales; different compounds).

The most promising techniques deployed so far are:

Semi-permeable membrane devices (SPMDs)
- research has been carried out to 'calibrate' them
- SPMDs have been used to show spatial and temporal trends (Meijer *et al.*, 2003)
- SPMDs have 'long' equilibration times (months/years)
- Interpretation of data is complicated by the presence of 2 phases (membrane and triolein) and the 'weathering' of the membrane which can occur over time
- SPMDs are expensive to use and analyse, and the clean-up and analysis is complicated (Petty *et al.*, 2000)

Polyurethane foam (PUF) discs
- The design and analysis is very straightforward; they are cheap, easy to construct, prepare and analyse (Shoeib and Harner, 2002)
- Initial studies have characterised their general performance and sampling rates
- PUF discs have been used for large-scale spatial mapping exercises in Canada and Europe
- Their ideal deployment times are typically weeks/months

Polymer-coated glass (POG) samplers
- This technique is very new, but shows considerable promise for short- and medium- time resolution deployments (weeks) (Harner *et al.,* in press)

XAD resin samplers
- o This technique utilises a 'high capacity' resin to sample the gas phase, and has been deployed on a regional scale study in North America (Wania *et al.*, in press). It shows considerable promise as a sampler. Potential problems may include ensuring low blanks and sample clean-up times

Given the tremendous potential of passive samplers for regional/global monitoring, it may be appropriate for UNEP to consider a small, specialist workshop to discuss the best options and a strategy to ensure their optimisation.

Vegetation
A number of studies have utilised vegetation as 'natural passive air samplers'. These include a number of national, regional and even global-scale studies. These are based on the principle that the vegetative surface is covered with wax/lipids, for which POPs have a natural affinity. A wide range of plant types has been used (e.g. pine needles, mosses and lichens; Calamari *et al.,* 1991; Kylin *et al.,* 1994). However, vegetation is not an ideal matrix for regional/global monitoring because:
- o There are large inter-species differences in air-plant POP transfer efficiencies
- o There are large intra-species differences in growth rates and plant condition regionally
- o There are wide differences in species range/habitat, so it is impossible to utilise the same species, or even the same type of vegetation over wide areas
- o Little information will be available about exposure time and it will probably be unclear whether the plant is kinetically limited or at equilibrium with the air
- o Some uptake of POPs from soils/dust, and the potential for photolysis/breakdown of POPs on plants can complicate data interpretation

Given that there are a number of 'man-made' passive air samplers now available, which offer a high level of 'control' in a study (i.e. deployment time/conditions), vegetation may not be the most appropriate medium for the UNEP project.

Soil
Soils are an important environmental compartment with respect to POPs. Key points for consideration include:
- o POPs accumulate in soils via atmospheric deposition, but are also deliberately applied to soils as pesticides, or in wastes (e.g. sewage sludge).
- o POPs have an affinity for soil organic matter (SOM) and are very persistent there. Hence SOM contains a large percentage of global burden of POPs.
- o Recent studies have shown how soils reflect large-scale spatial differences in cumulative atmospheric deposition/net air-soil exchange (Meijer *et al.*, 2002; Ribes *et al.*, 2002; Meijer *et al.*, 2003).
- o Archived soil samples have been used to show temporal trends of pollutants in the environment (Meijer *et al.*, 2001)
- o Soils are also very heterogeneous and the concentrations of POPs present will differ between ecosystem types. Hence, regional/global sampling programmes would need to address important questions of sample heterogeneity, soil/sample depth, ecosystem type etc.
- o Because of the persistence of POPs in soils, soil POP concentrations change very slowly (over years/decades). Monitoring programmes with soils would

therefore highlight the spatial variability of POPs. However, soils are an extremely difficult medium to sample, to demonstrate temporal trends.

In summary, it may be considered that background soils are a key medium to show the spatial distribution of POPs; however, time trend monitoring may be better achieved by focussing on other media.

Water
Considerations regarding water are as follows:
- o POPs are poorly soluble in water and therefore large volumes need to be sampled
- o Concentrations of contaminants are often highly variable in water bodies, varying with discharge conditions, season/time, depth etc.
- o Concentrations in rivers are strongly influenced by local discharges and conditions. Hence, they are not ideal for reflecting national/regional POPs usage
- o The dissolved phase/particulate phase distribution of POPs can be highly variable, dependent on particulate loading and temperature
- o Active sampling of water can be labour intensive, require specialist equipment and trained operators. There is also a high potential for sample contamination

In summary, it may be considered that active sampling of waters is not warranted under this programme.

Passive sampling of water
A number of programmes have developed techniques for the passive sampling of waters. Their main advantage over active-sampling are the time integration and the 'enrichment' of concentrations, making analysis easier. Techniques include:

SPMDs Originally developed for water sampling, SPMDs have been widely used (e.g. Granmo *et al.*, 2000). However, a number of problems have been identified (as noted above for air). In addition, SPMDs show a high susceptibility to biofouling and hence gross variations in uptake rates (Huckins *et al.*, 1999).

Mussels The 'Mussel Watch' programme was originally conceived to monitor heavy metals in coastal waters (O'Connor, 1994). However, it has also been utilised for the large-scale spatial mapping of POPs in coastal waters in North America. A number of studies have investigated the uptake kinetics and equilibrium status of mussels and other invertebrates. Mussels are quite ubiquitous, and therefore may provide a convenient and relatively easy way of conducting spatial/temporal trend studies of coastal waters.

Sediments
Continental shelf sediments contain a large percentage of the global burden of POPs. POPs reach shelf sediments via atmospheric deposition, riverine discharges, soil erosion/runoff etc. Undisturbed sediment cores can be used, in conjunction with radioactive dating techniques, to look for temporal trends in POPs, with a temporal resolution of ~5 years. Hence, sediments:
- o are generally an easy medium to sample and analyse for POPs
- o bulk samples provide a poorly defined 'time-integrated sample

- o tend to reflect local use patterns rather than global trends
- o are affected by changes in land use/hydrology, which can result in changes in sediment flux

Wildlife

Wildlife is a small but very important compartment for POPs in the global environment, and can be used to determine spatial and temporal trends of POPs in the environment (Braune *et al.*, 1999). POPs bioaccumulate in animals because of their high lipid content and their long lifetimes, and some POPs bioconcentrate up food chains, with very high levels detected in top predators such as polar bears, seals, whales and birds of prey. This is another of the main criteria governing the international control of POPs. Indeed, the levels in some top predators are high enough that toxic exposure effects are clearly observed (Bernhoft *et al.*, 2000). Species of wildlife have patchy distributions in the environment, with few species, if any, found all over the world. Therefore, in order to successfully utilise wildlife for monitoring trends of POPs in the environment, it is necessary to make a careful consideration of which species will provide most information. A key issue to consider is that some POPs are strongly degraded in animal cells. Some of the different media available are discussed below:

Bird eggs

Many bird species occur at the top of terrestrial or aquatic food chains, and therefore bioaccumulate large quantities of POPs, which are then passed on to eggs. These eggs have a high lipid content and therefore can contain large quantities of POPs, which means that detection limits for POPs are not normally a problem. Another important consideration is that bird eggs have been archived in some places and can therefore be used to calculate past trends as well as future ones. Birds eggs have proven to be very useful for mapping of both spatial and temporal trends of POPs on local and regional scales (e.g. Norstrom *et al.*, 2002). The biggest problem with this technique is that there is no single species of bird with a natural global distribution. Comparison between data from different species, or even data from the same species from different regions, is difficult because differences in food web structure will significantly affect POP accumulation. In particular, bird species feeding on aquatic food chains will have a very different exposure to those feeding on terrestrial food chains. A further problem is that metabolism of some POPs is known to occur in birds, and levels of these POPs in bird eggs will not exactly reflect environmental concentrations.

Marine mammals

Many marine animals, such as whales, seals and dolphins, have been found to have a very high burden of POPs (Aguilar *et al.*, 2002). These animals are generally near or at the top of aquatic food chains, and have large blubber layers that accumulate POPs. They have been successfully used for studies of temporal trends of POPs in the marine environment (e.g. Ikanomou *et al.*, 2002). A problem however with any mammal species is that metabolic activity is high, meaning that POP levels can be reduced by biodegradation. Further complications occur in that many species of marine mammals, in particular whales, migrate large distances and therefore don't provide good spatially-resolved data. Also, marine mammals have long life spans, in the order of decades, and therefore adults will have accumulated POPs over a long time period, making monitoring of short-term trends difficult. The use of young

animals is hampered by the fact that mothers pass on a large percentage of their burden to their offspring, in particular to the first calf, and that this has a significant effect on the POP burden throughout the animals life. It is likely, however, that if the mother's burden is depleted by this process, levels in subsequent calves should reflect more recent POP levels and therefore they could be of use for monitoring programs.

Foodstuffs

A number of domesticated animal species could also be used for studying spatial and temporal trends of POPs in the environment. Food produced from these animals would make a valuable monitoring tool, not only because domestic animals tend to have a much greater global distribution than wildlife species, but also because these food items provide a significant contribution to human POP exposure. Monitoring these foodstuffs will therefore not only give information on source reduction, but also on exposure reduction. Many countries already have sampling programmes of their foodstuffs for other purposes, which may be exploited. The available media are discussed in the following sections:

Milk and butter

These are key foodstuffs for many populations and often a major source of human exposure to lipophilic POPs. Butter has been used previously for a global POPs survey (Kalantzi *et al.*, 2001).

Advantages of these matrices include:
- o The high lipid content provides relatively high concentrations of most POPs, with good detection limits and relatively easy analysis
- o Milk can be taken from herds, at the dairy, and hence represent a highly integrated, homogenised sample from several cows/animals
- o The main source of POPs to the cow is usually grazing pasture or feed
- o The main source of POPs to pasture is atmospheric deposition. Hence, well chosen milk fat samples broadly represent/integrate atmospheric concentrations of POPs. Air-milk fat transfer factor data are available

Potential disadvantages include: the air-milk transfer is also influenced by temperature, soil ingestion, other feed constituents, animal husbandry conditions and the stage of animal's lactation cycle. In addition, some POPs (e.g. PAHs) may be metabolised in animals and therefore cannot be monitored in this way

Chickens eggs

Domesticated chickens are very widespread globally, and an important source of POPs to the diet. As discussed above, eggs may prove a useful monitoring matrix and such samples, if taken to a certain protocol, may provide an interesting biological monitoring tool.

Sampling human populations

There are a number of advantages to directly monitoring levels of POPs within the human population. Firstly, humans have a truly global distribution, which allows complete spatial mapping of POPs in the global environment. Secondly, a number of institutions possess archives of human tissue, which will allow measurement of POPs

from the past few decades, and increase the chances of detecting significant temporal trends. Thirdly, monitoring humans will not only give information about general levels of POPs in the environment, it will also directly show whether efforts to reduce emissions of POPs is having any affect on human exposure. Three tissue types are commonly analysed for POPs:

Blood
- o Human serum has been used for temporal trends (Dallaire *et al.*, 2002) and population studies (Schafer and Kedgely, 2002)
- o All 12 POPs can be measured in human blood (Schafer and Kedgely, 2002)
- o A method has recently been reported for simultaneously studying a wide range of POPs (Sandau *et al.*, 2003)
- o Most/all countries collect blood for other purposes, so a sampling infra-structure probably already exists
- o Ethical issues may need to be explored, as the donor's permission may be needed
- o Blood has a low lipid content and therefore reasonably large volumes are needed
- o Blood POP concentrations are variable in the short-term (e.g. influenced by recent food consumption). They are also variable in the population, depending on diet, weight etc.

Breast milk
- o Human milk has been widely used for spatial (Becher *et al.*, 1995) and temporal (Mes, 1994; Noren and Meironyte, 2000) trends
- o It has a high lipid content and therefore can be used to detect wide range of POPs
- o Milk gives information for a sub-section of the population
- o Concentrations vary, depending on the number of pregnancies, the stage of the lactation cycle and the mother's age/diet etc.

Human adipose
Adipose has been used previously (e.g. Covaci *et al.*, 2002; Choi *et al.*, 2003) for spatial and temporal trend studies, but collection is difficult.

Use of bio-indicators or bioassays
A number of bioassay tests exist, such as luciferase report assay, DNA microarray, and more, that estimate pollutant concentrations base on the strength of their toxicological effects (see Behnisch *et al.*, 2001 for a review of these techniques). These methods however are not chemical specific, with many individual chemicals eliciting similar responses. Indeed, when many chemicals are present, as occurs in all environmental samples, the test result gives a combined activity for all the chemicals present that cause the same toxicological effect. They are therefore probably not useful for the application of monitoring changes in levels of individual POPs, since declines in levels of POP chemicals could be masked by changes in levels of other chemicals. They could be useful, however, when combined with measurements of individual chemicals.

Site selection

Important decisions need to be made about the objectives of the programme, to determine the choice of locations. Some discussion points are as follows:

- o Background environments can be selected, to give information on regional trends. This would appear to be the *primary* purpose of the network. Should this be the focus of the network, or is there merit in including urban areas too?
- o Some POPs are primarily sourced in rural areas (e.g. pesticides), others are urban (e.g. PCDD/Fs)
- o Urban areas can be difficult to sample 'representatively', because there are numerous diffuse sources
- o Trends in terrestrial and aquatic systems may be different, receiving different inputs, and responding to source reductions at different rate

Monitoring sites would presumably have certain (minimum) requirements. For example, locations for air monitoring should be supported by: meteorological data, sample storage facilities (freezer?), and trained personnel to undertake sampling.

Sampling strategies
There are a few important issues that need to be taken into consideration when designing monitoring networks:

1. What are the advantages/disadvantages of pooling samples.
    -improves detection limits
    -smooths out short-term temporal variability e.g. from differing wind direction in air samples (Sweetman and Jones, 2000)
    -smooths out variability between individuals within a population (Kalantzi *et al.*, 2001)
    -lose information about emission fluctuations and point sources

2. The number of analyses required to detect trends;
    -depends what the analytical uncertainty is for each sample
    -the lower the concentration in the sample, the greater the analytical uncertainty
    -the bigger the uncertainty, the more samples are needed to reduce error bars

3. The frequency of sampling required to detect trends;
    -depends on what the temporal trend is
        -the smaller the loss half-life, the longer the interval needed between samples, and the longer the overall study period
    -depends what the error is for each data point
        -the bigger the error, the more time points required

4. Sampling should be designed to enable multiple analyses to be conducted
    -larger volumes of sample are required to detect certain POPs, e.g. dioxins
    -active air sampling should be designed to avoid breakthrough of more volatile POPs
    -collect lots of sub-samples for separate analysis or split extracts from individual samples

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-archive some of these for retrospective analysis

Comments on sampling techniques and the links to analysis

Once decisions have been reached about the choice of matrix/matrices to include in the network, a number of aspects of relating to the practicalities of running the network must be addressed. These include:

o How extensively should the network be 'co-ordinated'? For example, should the frequency, number, timing of samples be synchronised between countries, or is this unrealistic/unnecessary? One issue where this is particularly important is with air sampling. If samples are collected across hemispheres, for example, it will be 'summer' in one region whilst it is 'winter' in another. POP usage, emissions, and re-cycling are all temperature/seasonally dependent.

o How often (seasonally/annually/biannually?) should samples be collected (this is obviously matrix dependent)?

o Replicate sampling and pooling/bulking techniques are key to reducing the error bars in temporal trend studies.

o Additional replicate sampling should be done for some media, so that samples can be archived and be available for retrospective analysis.

o Important QA/QC issues arise at the point of sampling. For example, for air/water sampling, 'field blanks' are essential.

o What is the inter-relationship between sampling and analysis? Are regional laboratories being considered, to handle the samples from several individual countries/stations?

o A number of organisations have produced good advice on sample handling and storage, which can be used to develop protocols for the network.

o Sample transportation raises important issues, including:
> -are samples collected by an agent or posted to central office/lab by collector?
> -should samples be shipped frozen/refrigerated?
> -certification is required to ship certain matrices between countries

Existing monitoring networks and the linkages to modellers

Very valuable information can be obtained from the experiences of existing networks. Key amongst these are:

o Air monitoring networks: IADN in Canada/US (Buehler *et al.*, 2002); TOMPS in the UK; EMEP/AMAP experiences.

o Biological monitoring in the OSPAR region (Stagg, 1998), Baltic region (Bignert *et al.,* 1998) and the Great Lakes region (Norstrom and co-workers).

o Specimen banking/archiving in Germany (Oxynos *et al.*, 1994), Scandinavia (Lunden and Noren, 1998), Canada (Hobbs *et al.*, 2001) and the US.

A powerful link can be established between the measurement programme and modelling. A number of models are being developed to aid understanding of the regional and global fate of POPs in multi-media environments. They can provide context, to aid decisions about key media (air; soil; sediment, for example), expected rates of change and – hence sampling frequency.

A suggested approach
To stimulate workshop discussion, we offer the following suggestions:

1. Air monitoring <u>must</u> be a key feature of the global programme.
   a) Active air sampling <u>should</u> be conducted at a number of 'master stations' based at meteorological/research stations, located in background environments in different regions of the world. These would monitor for seasonal and annual trends of POPs.
   b) A much more extensive passive air-sampling network <u>should</u> be established. This would address the spatial variability of airborne POPs in the global regions. Such samplers would be used to take 'integrated' samples through the year (e.g. 3-6 monthly exposure times), and could be placed at background <u>and</u> urban/source locations.
   c) A specialist workshop <u>should</u> be convened to advise on the most appropriate passive sampler design for the programme.

2. Coastal waters <u>could</u> be monitored, by a co-ordinated 'Mussel Watch' programme. Sampling could be undertaken on a timescale of the order of every 2-3 years.

3. The link between emissions and human exposure <u>should</u> be monitored, by a programme sampling cows milk fat/butter, or chickens eggs. Integrated sampling/pooling of such media will provide a relatively cheap, highly integrated sample. They will indicate broad spatial and temporal trends. Samples taken yearly/biennially, for example, should show a response to air emission source reduction. These media would also highlight where other inputs to the foodchain may be occurring (e.g. contaminated feeds), which can subsequently be addressed by specific source identification/reduction.

4. Wildlife exposure <u>could</u> be monitored, by a co-ordinated programme aimed at a widely distributed species. e.g. sea gull eggs; grey seal blubber. Such samples should be selected from specific colonies/populations, constrained as to age/sex where possible (to reduce variability), and sampled every 3 years, for example.

5. Global patial surveying of POPs <u>could</u> be addressed by a co-ordinated programme of background soil (terrestrial) and sediment (aquatic) sampling. However, such media are heterogeneous and have long response times (decades), so they are not good media for temporal trend monitoring.

6. Spatial and temporal trends in human exposure <u>should</u> be monitored, through analysis of blood or breast milk. Sampling programmes can be developed, with reference to extensive ongoing national monitoring programmes.

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UNEP Workshop to Develop a Global POPs Monitoring Programme to Support the Effectiveness Evaluation of the Stockholm Convention

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Quality Assurance/Quality Control and Data Treatment

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Abstract

QA/QC requirements are being discussed with regard to the Global network for the Monitoring of Chemicals in the Environment (GMN) by UNEP. Certified reference materials (CRMs) are available for a number of POPs and are recommended to check the accuracy of the analysis. The long term reproducibility of the methods should be checked by the use of laboratory reference materials (LRMs). Interlaboratory studies may be beneficial for the training of laboratories. For most POPs proficiency tests are available on an annual or even a more frequent basis. Guidelines should be prepared to advise laboratories on sampling procedures and analytical methodologies. Single laboratories may be in a better position to detect time trends compared to groups of laboratories, although the risk of bias is obviously greater. All data produced in a monitoring programme should be checked on QA/QC before they are stored in a database.

Introduction

UNEP has initiated a Global Network for the Monitoring of Chemicals in the Environment (GMN), with the aim to obtain comparable data for levels or impacts of hazardous substances in the environment from different parts of the world to find possible spatial and/or temporal trends. In that way the effectiveness of the implementation of the conventions will be monitored, as well as the possible decreases of environmental contaminant levels. An Advisory Group, established in May 2002 to further develop the programme, endorsed a Workshop to discuss and underpin the development of monitoring programmes, particularly in developing countries. One topic of this Workshop will be the quality assurance/quality control (QA/QC) and data treatment, which will be discussed in this background document.

The persistent organic pollutants (POPs) discussed in this document are: aldrin, cis- and trans-chlordane, dieldrin, chlorinated dibenzo-*p*-dioxins and furans, DDT, endrin, heptachlor, hexachlorobenzene (HCB), mirex, polychlorinated biphenyls (PCBs), and toxaphene (chlorobornanes).

Over the last two decades QA/QC procedures for POPs have developed, both within laboratories and in connection with international monitoring programmes. Key elements in QA/QC are the use of reference materials, the use of quality charts, participation in interlaboratory studies and the use of guidelines for sampling and analysis. This document will discuss the i) availability of suitable (certified) reference materials (CRMs) for the POPs involved, ii) the need for interlaboratory studies in a training phase, as well as the need for proficiency testing in parallel with the monitoring activities, and the availability of such programmes, iii) the required quality of the data to enable the determination of temporal and spatial trends, and iv) the design of one or more databases for storage of the data.

Reference materials

Reference materials are essential for monitoring the quality of the analysis in a laboratory. Internal or Laboratory reference materials (IRMs or LRMs) are large, homogeneous batches of a representative matrix, of which a sub-sample is analysed in each series of samples. The results for the target compounds are plotted in a quality (QC) chart, which enables the evaluation of the long-term reproducibility of the method. Deviations from the mean of this chart (determined after at least 10 measurements) give information on the quality of the method. Significant deviations (more than 3 standard deviations) lead to non-acceptance of the data produced in the series of samples analysed. Smaller deviations will lead to action in the laboratory to improve the analytical method. These QC charts are a very valuable tool to maintain the quality of the analysis. They are nowadays considered to be an essential part of QA/QC procedures in laboratories. Accreditation of a laboratory is not possible without the use of QC charts. The obvious drawbacks are the time and costs involved in the maintenance of such a system. In case a laboratory analyses different matrices, different LRMs will be needed. In case various compounds are being analysed, QC charts for each compound are normally required. In some cases, e.g. for PCBs compromises, e.g. selection of a sub-set of congeners, may be acceptable. Laboratories involved in the UNEP GMN should apply the QC charts for the analyses of the POPs. The central preparation of large batches of LRMs in order to provide a number of or even all participating laboratories with the same material may be considered, with the aim to assist laboratories who would not be able to prepare homogeneous LRMs by themselves.

Another essential QC tool is the use of CRMs. A CRM (also known as standard reference material or SRM) is defined as a reference material, one or more properties of which are certified, with a stated uncertainty, by a technically valid procedure, which are traceable to a stated reference and accompanied by a certificate or other documentation issued by an accredited body, to be used for the evaluation of the accuracy of the method(s) used by the laboratory (Anon., 1981, Quevauviller et al., 1999). So, a CRM is used to assess if the method used provides a true value. Per method, a CRM is normally analysed a few times per year. The trueness of the CRM is normally obtained by a group of expert laboratories who work together in an interlaboratory study which has to fulfill very strict criteria. The data produced in such a certification exercise are subsequently judged by another group of experts (certification committee), after which a certificate will be made. There is only a limited number of bodies in the world able to provide CRMs. These include the European Union (Bureau Communautaire de Référence (BCR), Brussels, Belgium), the National Institute of Standards and Technology (NIST, Gaithersburg, USA), the National Research Council (NRC, Canada), and a few commercial organisations. The quality of the produced CRMs differ between the certification bodies, which has of course implications for the specific use of CRMs. The quality of CRMs is regularly discussed between the certification bodies, e.g. at the conferences for Biological and Environmental Reference Materials (BERM), which are being held every three years.

Because of the strict requirements, the production of CRMs is expensive. This is particularly true for POPs, as analytical methods for POPs are normally complex and time consuming. Consequently, the number of available and suitable CRMs for POPs in environmental matrices is limited. De Boer and McGovern (2001) have given an overview of available CRMs for POPs in biota and sediments. A summary of that overview is shown in the tables 1 and 2. For a number of POPs, aldrin, endrin, and

toxaphene in biota and sediment, and dieldrin, mirex and trans-chlordane in sediment, CRMs are not available. For some of these, apart for toxaphene, indicative (non-certified) values have been given in some of the CRMs mentioned in the tables 1 and 2. These indicative values allow the alternative use of these CRMs, in absence of certified values for these POPs. As stated above, also the quality of the CRMs in the tables 1 and 2 may not be equally good. Additional difficulties are found in limited transport possibilities, such as is the case fore the SRM 1945, whale blubber, which, due to legal transportation limitations for marine mammal tissue, cannot be sent to Europe, and SRM1974a, a wet frozen mussel tissue, which is also not sent to Europe, presumably due to high costs involved. The CRMs for biota are often freeze-dried materials, which have the drawback of not being suitable for testing the extraction part of the methods. Recently, fresh, sterilised materials have been made available by BCR (BCR682 and 718). All sediment CRMs are (freeze-)dried materials. Some commercial sources (Cambridge Isotope Laboratories, USA, Laboratory of the Government Chemist, UK) provide CRMs for POPs, but often the values are indicative, or the materials have been spiked at an unrealisticallly high level, or the exact nature (fish species) is unknown. In spite of these disadvantages, these materials may serve as an alternative in absence of good CRMs for

Table 1. CRMs for POPs in biota

CRM		c-C	t-C	diel	diox/furan	DDT	HCB	mirex	PCB
SRM1974a	mussel	X	X			X			X
SRM1588a	cod liver	X		X		X	X		X
SRM1945	whale bl.	X				X	X	X	X
SRM2974	mussel	X	X			X			X
SRM2977	mussel	X		X		X			X
SRM2978	mussel	X	X	X		X			X
140/OC	plant			X		X			X
BCR598	cod liver	X	X	X		X	X		X
CARP-1	carp				X				X
BCR349	cod liver								X
BCR350	mackerel								X
BCR682	mussel								X
BCR718	herring								X

c-C: cis-chlordane, t-C: trans-chlordane, diel: dieldrin, diox/furan: chlorinated dibenzo dioxins and furans.

Table 2. CRMs for POPs in sediment

CRM	c-C	diox/furan	DDT	HCB	PCB
SRM1944	X		X	X	X
SRM1939a	X		X		X
IAEA383					X
IAEA408			X	X	X
HS-1					X
HS-2					X
BCR536					X
DX-1		X			
DX-1		X			

c-C: cis-chlordane, tdiox/furan: chlorinated dibenzo dioxins and furans.

some POP/matrix combinations. The PCBs in tables 1 and 2 refer to chlorobiphenyl congeners (CBs). The number of CBs certified varies per CRM. This is also true for the dioxins and furans. Some additional CRMs have been certified for total PCB. One CRM, BCR719, a wet, sterilised freshwater fish (chub) matrix, has been certified for four non-ortho substituted (dioxin-like) CBs (congeners 77, 81, 126 and 169). DDT normally includes p,p'-DDT, p,p'-DDD and p,'p-DDE, and sometimes, in addition o,p'-DDT, o,p'-DDD, and o,p'-DDE. Clearly, several CRMs will be needed to cover all POPs, while for some POPs no CRMs are available. Official requests of international organisations such as UNEP to certifications bodies like BCR (Institute for Reference Materials, Geel, Belgium) and NIST, may stimulate the production of enough high quality CRMs for POPs. This is also true for contaminants which are not yet at the official POP list, such as brominated flame retardants, and for which CRMs are also not available, although many laboratories are developing analytical methods for these compounds or have started monitoring programmes.

For matrices other than sediments and biota, such as air, water and human tissue or blood, no CRMs can be found in the catalogues of NIST and BCR.

Interlaboratory studies

Although CRMs can be used to check the accuracy of the method, participation in interlaboratory studies is needed for additional checks. One argument is that the target concentrations of CRMs are always known, and the advance knowledge may bias the analyst. Secondly, interlaboratory studies normally provide a wider selection of matrices and a wider range of analyte concentrations, which will help to ensure the robustness of the method. Finally, interlaboratory studies will enable a comparison of the participant's method with that of other laboratories. Some interlaboratory studies are specially designed for training of laboratories. Others are so called proficiency tests which are being organised on a regular basis as a service for laboratories to maintain the quality of their analytical methods. Participation in such proficiency tests is normally a requirement for accreditation. A number of ongoing interlaboratory studies would be suitable to serve for training of laboratories in POP analysis, as well as for proficiency testing in parallel with the monitoring activities.

Interlaboratory studies for POPs have been developed since the late 1970s. Some of the first studies were organised by the International Council for the Exploration of the Sea (ICES), Copenhagen. Soon, it was observed that one-off interlaboratory studies were of little value. These first exercises often resulted in a wide range of results, while later repetitions did not show any improvement. Stepwise designed interlaboratory studies, also organised by ICES, were more successful. A group of experts was responsible for the design of the exercise and for scientific advice to the participants, and objectives and targets for analytical performance were identified (Nicholson, 1989, Wilson, 1979). This advice helped participants to improve their methods and to obtain better results. The first stage of such a study normally focussed only on the analysis of a standard solution. Later steps were gradually made more complex: analysis of clean extract, analysis of raw extract, and analysis of real matrix. In this way the specific problems of the various steps of the analysis could be discussed. Because of the complexity of the POP analysis, this model proved to be successful. Between-laboratory standard deviations of for example CB analysis could significantly be reduced (de Boer et al., 1992, 1994, 1995). This model was also used within the QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe) programme (Wells et al., 1997). An additional

improvement of this programme was the organisation of dedicated workshops. At those workshops all analytical details were discussed, following a first exercise in which participants had often made various mistakes. The laboratories were assisted, by means of a stepwise designed study, to build up their method and reach a good comparability with other participants. This approach was for example successfully used for the analysis of toxaphene (de Boer et al., 2000), and is currently being carried out for brominated flame retardants.

Proficiency tests a being organized by various national and international organisations. A series of five proficiency tests for trace metals and a number of organochlorine pesticides in food was organised in 1993 and 1994 by the Global Environmental Monitoring Scheme (GEMS) of the World health Organisation (WHO) (Weigert et al., 1997). These tests, which were carried out according to the international harmonized protocol for the proficiency testing of chemical analytical laboratories (Thompson and Wood, 1993a,b), showed that of the 136 participating laboratories only 41% were successful for organochlorine pesticides analysis. This indicated that care is needed in the collection of data from monitoring programmes, and also the need for further measures to improve the performance of the participating laboratories. The proficiency tests based on the international protocol mentioned above are based on the use of so called Z-scores. Z-scores show the deviation of a participant's result from the mean value, in relation with the in advance defined acceptable standard deviation. A Z-score between –2 and +2, i.e. a result within 2 standard deviations from the mean value, is considered as acceptable, a Z-score between –2 and –3 and between +2 and +3 is considered as questionable, and a Z-score <-3 or >+3 is considered as unsatisfactory. The target standard deviations and Z-scores can either be based on the mean value of the entire data set, after exclusion of extreme outliers, or be based on the results of a group of expert laboratories, which were selected on the basis of previous excellent results and good results with CRM analysis. The sum of Z-scores can be used to follow the laboratory's long-term performance. This system of Z-scores has also been used in the proficiency tests organised within the QUASIMEME programme. Over 200 laboratories participate in this programme on an annual basis, in proficiency tests on nutrients, trace metals, organic contaminants, shellfish toxins, dioxins and furans, and other groups of analytes in marine matrices (water, biota, sediment). For most organic contaminants, participating laboratories receive twice per year two or three samples, in which they should determine the various compounds. Co-parameters such as dry weight and total lipid content can be analysed as well. The programme is mainly designed to serve laboratories active in the Joint Assessment and Monitoring programme (JAMP) of the Oslo and Paris Commissions. However, laboratories active in other monitoring programmes, such as under ICES or the Helsinki Commission (HELCOM), or the Arctic Monitoring and Assessment Programme (AMAP) (Asmund and Cleemann, 2000), also participate in this scheme. Because of the regularity of this scheme and the good results achieved until now, further discussions on this topic could consider the use of the QUASIMEME programme as a service to the UNEP GMN. Dependent of the group of candidate laboratories, it should be decided if a (stepwise designed) training programme will be required, prior to the proficiency tests which should be carried out in parallel with the monitoring programme.

Many other interlaboratory studies have been held for POPs. One further example is the WHO-coordinated study on chlorinated dibenzo-*p*-dioxins and furans (fourth round) (Anon., 2000). In this study specific criteria for acceptance of laboratories were set for the deviation of the consensus value and the coefficient of variation. Only

laboratories fulfilling all quality criteria were accepted to carry out monitoring studies for the WHO. In this round only one out of 21 laboratories laboratory was accepted, which clearly shows the difficulties for laboratories in dioxin and furan analysis. Proficiency tests for dioxins and furans in food are being organized on an annual basis by the Norwegian Institute for Public Health, Oslo (Småstuen Haug et al., 2002). Since a few years interlaboratory studies for PCBs and some organochlorine pesticides in human tissue and blood are being organised within the framework of the Arctic Monitoring and Assessment programme (AMAP) by the Institut National de Santé Publique du Québec (Weber, 2002). Interlaboratory studies in other matrices such as air and water are rarely being organised.

Since the last decade developmental work has been carried out on the use of passive samplers or semi-permeable membrane devices (SPMDs), both for water and air. These systems may be beneficial for the measurement of time-averaged concentrations of POPs. However, calibration of these systems is complicated and may differ per system. Large-scale interlaboratory studies have not been carried out, but good QA/QC work has been carried out in some specific research projects (Kingston et al., 2000, Booij et al., 1998, McCarthy and Gale, 2001, Bergqvist et al., 1998).

Quality of data

The quality of the produced data is dependent of a variety of parameters. All parameters involved should be considered in a set of guidelines, in which recommendations should be given on how to optimize the sampling and analysis methodologies. An example of such guidelines are the JAMP guidelines for monitoring of contaminants (Anon., 1997). These guidelines give detailed information on sampling procedures for various types of biota, on storage conditions and pre-treatment of samples, on analytical methods, such as calibration of instruments, calibration solutions, extraction and clean-up conditions, injection techniques, column conditions for gas chromatography (GC), and detection techniques. In addition, a set of quality assurance parameters is described: system performance, recovery, blanks, detection limits, and use of LRMs and CRMs. Such a set of guidelines will be essential for an optimum performance of monitoring programmes.

The key question with regard to quality of data is: How accurate should they be? Obviously, they should be accurate enough to identify changes in temporal or geographic trends in contaminant concentrations. Two situations should be considered to answer this question in more detail: i) accuracy in one laboratory, and ii) accuracy of results of a group of laboratories. Nicholson (1989) gives an examples for one laboratory. For a true concentration μ, a precision σ, a bias $\pm b$, and a normally distributed data set, accuracy is defined as being 95% sure that a result will fall in a range with upper limit L_U and lower limit L_L. Then these limits, the true value, and the bias are related by the equations

$$L_U = \mu + |b| + 1.645\sigma$$
And $$L_L = \mu - |b| - 1.645\sigma$$

As a percentage of the true value, accuracy is given as:

%accuracy = $100(|b| + 1.645\sigma)/\mu$

Assuming that a target accuracy for a certain monitoring programme would be 5%, it can be calculated on the basis of the bias and precision of a method, which can be obtained from duplicate analyses and quality charts, respectively, if a method of a laboratory is suitable to detect the target change in trend of 5%. For example, a method with a mean value for an LRM of 88 μg/L, a bias of 5.4 μg/L and a precision of 5.1 μg/L would result in an unacceptable accuracy of 16%, while a method with a mean of 87 μg/L, a bias of 0.57 μg/L and a precision of 0.50 μg/L would result in an acceptable accuracy of 1.7%.

As soon as a group of laboratories is involved, the accuracy will increase due to a basic statistical principle (Nicholson, 1989). Consequently, the accuracy obtained by a group of laboratories will always be larger than for an individual laboratory. De Boer et al. (1994) concluded that in an interlaboratory study on CBs, with 35 participating laboratories, the best result was obtained for CB 118 (2,4,5,3',4'-pentachlorobiphenyl) in a cleaned seal blubber extract with a reproducibility of 2 (CV 24%). This indicated that the differences of two values in one similar sample determined by this group of laboratories would be within a factor 2 with a probability of 95%. In this way a reliable indication for the performance of a group of laboratories is obtained, but it is clear that such a result is not very useful for trend studies. The relatively new statistical method of Cofino et al. (2000) may be useful for a better understanding of a data set and particularly for not normally distributed data sets. This method may lead to a lower estimate of the accuracy that can be obtained by a group of laboratories, but a substantial number of laboratories may sometimes not be included in the final data set as they may have caused a bimodal distribution. Recent QUASIMEME data treated by this method show coefficients of variation of ca. 15% for CB 153 and p,p'-DDE corresponding with a reproducibility of 1.5, but of >100% corresponding with a reproducibility of >6.5 for some other organochlorine pesticides (de Boer and Law, 2003). The group of laboratories with this performance would be able to detect changes in trends of ca. 50% for CB 153 and p,p'-DDE, but only changes in trends of an order of magnitude for some organochlorine pesticides. Only in areas with relatively high POP concentrations, a better performance may be expected. So, even by using a more advanced statistical technique, it is concluded that the performance of a group of relatively experienced laboratories is not good enough to detect changes in trends of POP concentrations which are smaller than 50%. The use of individual (expert) laboratories for this purpose may therefore be more beneficial.

A final quality aspect is the detection limit. According to the current state-of-the-art laboratories should be able to establish a detection limit for their OCP and CB analyses of ca. 0.1 μg/kg wet weight per compound or congener. For dioxins and furans, it should be possible to establish detection limits of ca 0.1 ng/kg. The JAMP guidelines mention a detection limit of 0.2 μg/kg for OCPs and CBs (Anon., 1997). It may be discussed how non-detects are being used in the database. Hoogerbrugge (2000) mentioned that the imputation of half the detection limit values showed a remarkable improvement compared to the options of using the detection limit value or using zero values.

Data presentation

Before including results of a monitoring programme, it should be checked if the data delivered have passed all the quality criteria. Were the recoveries OK? Was the result of the LRM in the sample series within two standard deviations of the mean? Has the laboratory participated in a proficiency test for this compound? Has a CRM been

used? The producers of the data may be asked to complete forms in which answers to these and other questions related to QA/QC can be answered. Subsequently, these answers should be checked, and only if data fully comply with the quality criteria, the data can be accepted for storage in the database. It may be desirable to flag data according to different quality objectives. Such procedures are for example followed by ICES when collecting data of the JAMP for the Oslo and Paris Commissions. In that case all data from different regions in the north-west Atlantic are collected, checked, and centrally stored in a database. The final quality checks are being carried out annually during a meeting of a QA/QC committee. Alternatively, regional databases could be used, which may be checked by audits from a central office.

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Data Communication

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Abstract

This chapter will describe:

1. Identification of objectives on data communication
2. Review of existing data communication examples
3. Problem identification for existing data communication systems
4. Technical points for the data and metadata structures
5. Development of example format of standardized database for warehouse
6. Summary

The goal of this chapter is to provide a basis for discussing issues surrounding the management and use of a POPs data warehouse, such as required reporting format, database structure, concerning topics on data sharing including the ownership/intellectual right on data and presentation methodologies. Review of existing programs will assist in this discussion, and strategies for future, more sophisticated, communication methodologies will be discussed.

Identification of objectives on data communication

Background of data communication
The results from the global POPs monitoring programme will be used to determine
trends from monitoring POPs globally to support the effectiveness evaluation of the
Stockholm Convention. Effective data sharing among relevant bodies by consistent
data communication methodology is essential to achieving this objective.
Global monitoring data may be reported using wide variety of formats, from
appearances, contents to technical information levels and styles. Definition for
standardized format will be very important to develop a better data warehouse that can
be useful for the purpose of effectiveness assessment.
The authors believe that technical details could be important topics of discussion,
because the clear definition of data structure is essential to the development of well-
organized databases. Technical issues in this session should not only be considered
from an information technological point of view, but also from the point of view of
relevant scientific disciplines; including analytical chemistry, environmental science
and effectiveness assessment. This implies that close discussion and information
sharing with other technical workgroups will be essential to achieving the most
fruitful result.

General goal of data communication discussion
The phrase "data communication" implies a wide variety of concepts. This fact puts
this topic at risk of including too many issues and not resolving them. Therefore, the
authors suggest that the general goal of this discussion should be focused on *the
development of a well-organized data warehouse that contains databases of POPs
global monitoring data for the purpose of the planned effectiveness evaluation.* The
authors acknowledge that other possible uses of warehouse databases should be kept
in mind, however, topics implied in data communication, such as risk communication
or other more social issues, may need to be considered in depth at a later time.

The following background paper will focus on the technical methodologies for data
warehouse design and development and effective reporting of warehouse contents.
Possible target issues are identified as follows:

Development of data and metadata structures for effective communication
It may be difficult to obtain well-harmonized analytical data as a basis of a data
warehouse, because of the variety of analytical methods, sampling protocols and
QA/QC practices among data sources. We need to determine the minimum set of
metadata elements that would ensure the quality and consistency of data stored in this
data warehouse and a suitable data structure for that purpose.

*Development of methodologies for collecting and storing all data from participating
countries*
Some participating countries have developed electronic databases to store monitoring
data, however others have not. Also there are international programmes that have
developed electronic databases for the purpose. All data from participating countries
and international programmes are a valuable part of the POPs database whether
electronic or hard copy. Electronically-stored data can be linked by building a new
database and migrating data into it or by virtually linking the existing databases
together to form a warehouse. Non-electronic data presents a different set of

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problems. If a new centralized POPs database is developed, data entry mechanisms can be included that would allow the conversion of paper copy to electronic data. Manual data entry can be very costly, so we may wish to consider ways to include non-electronic data in summary reports without manually entering each value into a database.

Development of effective strategies to share information with the public
Sharing data electronically, through the Internet, is probably the most efficient way to provide information to assessors, stakeholders and the public, however alternatives must also be considered. The advantage of allowing access to a data warehouse via the Internet is that the data is available on demand. Users of the data can access only the portions that they want and can have both summarized/interpreted information and raw data. This type of access is excellent if all data in the database is electronic. If some is not, then the Internet presentation of the data is not complete. Written reports that explain the data as well as present summarizations are costly, but allow a more controlled release of information and allow non-electronic data to be included, presenting a more complete picture. These reports, along with summarized or raw data can be distributed via compact disc (CD or DVD) or by hard copy. This type of distribution, by its nature, limits access to the number of copies of a document or a CD that can be produced. Careful consideration on the ownership and/or intellectual property rights should be placed for the use of data, maybe depending on the strategies to share information.

Development of effective strategies to present data to the public
Whether data is shared electronically of in hard copy, there are two basic ways it can be provided, as raw sampling data or as summarized data. Raw sampling data can be provided electronically as files to download or in tables to examine on the screen or on paper. Summarized data can be displayed using tables, charts, graphs and Geographic Information System (GIS) technology. Using a GIS display has the advantage of providing almost "instant" understanding of place-based data by the general public. It allows different types of information to be displayed at the same time, thereby developing a picture of conditions. However, care must be taken when using this tool. There is a tendency to over summarize on a map, so the results can be deceiving. Statistical presentations using tables, charts and graphs also have these same problems and can be just as visual depending upon how they are used.

Development of strategies for building a data warehouse containing monitoring data that could be assumed to have consistent properties and qualities
It is expected that a data warehouse will contain several sets of databases containing different types of data. Some topics for discussion in this area would include the most effective way to design a data warehouse from a technical point of view, the pros and cons of centralized vs. dispersed system structure and strategies for storing and presenting data in a consistent manner.

Review of existing data communication examples
Many other organizations at various levels, from the research and national to the level of international collaboration have attempted to gather and disseminate monitoring data effectively. A major objective of our discussion is the development of a data warehouse in response to the requirements from the POPs convention. To that end, we have targeted examples of data warehouses that are currently providing access to

data and metadata electronically, through the Internet.   The purpose of this section is to allow consideration of effective data management/communication and take advantage of the successes of others. There are likely many more databases and data warehouses that could have been reviewed. In addition effective examples of communications may also exist in documented reports or other hardcopy formats, and the inclusion of this type of information in the expected data warehouse may be a topic of discussion. Additional examples can be discussed at the workshop.

The International Council for the Exploration of the Sea (ICES) has been developing a monitoring database for more than 2 decades. ICES Environment data center (http://www.ices.dk/env/index.htm) has been collecting marine contaminants and biological effect data from 19 member countries and its reporting format is used for reporting data for AMAP, OSPAR and HELCOM commission. The reporting format and coding system are shown on their website (http://www.ices.dk/env/repfor/index.htm). This format is well-organized and detailed for marine samples including biota, sediment, seawater, and recently biological effects (EROD and DNA adducts). The format includes the meta data information concerning sample nature and analytical protocols.

AMAP (Arctic Monitoring and Assessment Programme) is showing a data collection of POPs monitoring data (http://www.amap.no/data-gis/data-gis.htm). Although the web-based presentation is under development, example data is already presented on the website. The example data shows mean and range of measured data for each sampling point for each river.

EMEP (Cooperative Program for Monitoring and Evaluation of Long-Range Transmission of Air Pollutants in Europe under Convention on Long-Range Transboundary Air Pollution) also has activities on collecting POPs monitoring data, however, there is no web-based presentation of the data as yet.

UNEP GEMS/Water (Global Environmental Monitoring System/Freshwater Quality Programme) has been working on the data compilation and presentation of the monitoring data for water and food environment. UNEP GEMS/Water website (http://www.cciw.ca/gems/gems.html) has been showing monitoring data for physical/chemical pollution parameters, major and minor ions and organic contaminants, including POPs. The presentation format is somewhat simple, but the regional coverage is 69 countries over world.

The US Geological Survey has multiple databases. One of the most extensive is the National Water Information Survey (NWIS) (http://waterdata.usgs.gov/nwis). This database largely concentrates on surface water flows and ground water levels, however it has significant information on water quality. This portion of the database provides chemical and physical data on lakes, streams, springs and wells. It displays data based upon the sampling sites, but allows searches for sites bases upon contaminant type. The user of this site could find all of the sites, which were monitored for a particular type of contaminant, such as Organics, Inorganics, Biologicals etc. The results page lists the actual contaminants, but searches can only be performed by type. NWIS also displays its water flow data in a GIS format. (http://water.usgs.gov/realtime.html). The map is continuously updated directly with information form monitoring stations. This real-time data display may not be practical for contaminants, however, the way the data was displayed could be used. Sampling stations were color coded to indicate high, normal or low water flows, so areas of the US that are experiencing exceptionally wet or dry conditions could be determined at a glance.

NWIS is similar to STORET, owned by the US Environmental Protection Agency (http://www.epa.gov/storet/dbtop.html), however STORET lacks the sophistication in queries and data display. STORET contains raw biological, chemical, and physical data on surface and ground water collected by federal, state and local agencies, Indian Tribes, volunteer groups, academics, and others. All 50 States, territories, and jurisdictions of the U.S., along with portions of Canada and Mexico, are represented. Each sampling is accompanied by information on where the sample was taken (latitude, longitude, state, county, Hydrologic Unit Code and a brief site identification), when the sample was gathered, the medium sampled (e.g., water, sediment, fish tissue), and the name of the organization that sponsored the monitoring. In addition, STORET contains information on why the data were gathered; sampling and analytical methods used; the laboratory used to analyze the samples; the quality control checks used when sampling, handling the samples, and analyzing the data; and the personnel responsible for the data. Both NWIS and STORET have a data download feature. NWIS offers a few more options for the file formats.

The US Environmental Protections Agency has several other public data bases that contain information about toxic chemicals. Ecotox, (http://www.epa.gov/ecotox) provides the user with abstracts of toxicity studies by species, chemical, habitat or effect.   The Toxic Release Inventory (http://www.epa.gov/tri) provides information on chemical release into the environment and is similar to Canada's National Pollutant Release Inventory (http://www.ec.gc.ca/pdb/npri/npri_home_e.cfm). Both TRI and NPRI allow queries by location, pollutant and sampling year. The Canadian site presents results in an easy to read tabular format which allows drill down to each facility, if the search resulted in more that one facility. The facility page offers a second table with a complete record of the facility for the year in question. The data is also presented as a bar graph. USEPA TRI also presents data in a tabular format, but offers several different choices on the front page. Reports can be generated that focus on chemical, facility, geography or industry. In addition there is a trend report that displays total emissions over time. Drill downs from these reports are to metadata (definitions of terms, guides to interpreting the data etc.) None of these sites display data on maps.

Envirofacts (http://www.epa.gov/enviro) displays US EPA data in a GIS format as well as in tabular form. Envirofacts is a large data warehouse that combines information from a number of EPA databases. Envirofacts is extremely "place based" (facility, county, state). Most queries do not permit searches by chemical, even though some of the results display chemicals. The maps on this site, some of which are interactive, are excellent. However, it is difficult to find the chemical information in the tabular displays. The actual chemical released and the amount of the release are two pages away from the first table.

Problem identification for existing data communication systems
This section reviews some problems with existing systems. ICES could be used as a reference or guide for developing a data reporting format, since ICES includes the major metadata items especially concerning the nature of the sample and analytical protocols. However, ICES does not contain information, which describes whether or not a particular sample is representative of conditions in the area. This may be important information, when conducting an effectiveness assessment.

The UNEP GEMS/Water database has a great deal of data but with less information on metadata. This may be due to the fact that the major monitoring items are physical/chemical water quality parameters, which have harmonized sampling and

measurement protocols nearly everywhere in the world. Environmental monitoring for POPs may require a larger variety of metadata information, so the discussion on this topic may be more important for POPs monitoring.

One problem with the way data is displayed on some of the Internet sites mentioned above is the focus on the sampling site as opposed to the sampling results. While it is critical to have information about the site where monitoring is performed, displays of data also need to include summaries of data with a chemical focus. Canada NPRI and USEPA TRI do this better than other sites. The use of graphs, in addition to tables and maps would also add to the visual understanding of the data.

Most sites offered links to metadata. STORET and NWIS had the most extensive data in this area, which included analysis information, limits of detections and other quality control information. Other sites focused more on definitions of terms and data interpretation, than on the quality control aspects of individual samples taken. I could not determine whether it was because this information was not available or because it was not considered important. Quality control information was often not displayed with the same attention to formatting and readability as the other information available on the site. It was often difficult to read and difficult to find. The more technical the metadata was, the more it was buried.

Technical points for the data and metadata structures
Discussion points on numeric data properties
Effective digit information
Accurate storage and display of numerical data is critical to the effective usage of any analytical data. The database should not store a single digit after the decimal if the sensitivity of the analysis was actually to two places and conversely the database should not store or display two places when the accuracy was one or none. Data handling schemes in major database management software do not always explicitly recognize effective digit information of the numbers. Topics to be discussed here could be strategies for accurate capture of data from the original report and management of numeric data when databases that handle this information differently are joined to make a data warehouse.

Unit information
The unit of measurement is an essential part of analytical data. If analytical data are not accompanied by correct unit information, the numeric data can never be interpreted. The International System of Units (SI) has become a standard, however, there are similar systems that can cause a great deal of confusion. Example of these are "mg/L vs. g/m^3", "mg/g vs. mg g^{-1}" that use slightly different notations to express the same amount. In addition to the confusion caused by differing notations there is also confusion caused by the basis for the analysis, for example, dry vs. wet, lipid vs. whole-body, volumetric vs. weight and so on. In these types of cases, simple conversion between different unit systems may be difficult without additional information like wet-content, lipid-content or specific gravity and so on. The handling of analytical units can cause a great deal of technical difficulties, misunderstandings and additional work.

Topics for discussion in this area include: (1) Should we define a limited number of specific unit systems for each media/sample type? or (2) Should we accept any unit system without modification but with necessary relevant information? Intermediate solution between (1) and (2) may be possible. It may be very difficult to select

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specific unit systems as the appropriate ones for each specific media/chemical/sample combination?

LOD/LOQ information
Limit of detection (LOD) and limits of quantification (LOQ) are both essential information associated with analytical results. All analytical data should be accompanied by relevant LOD and LOQ information as numeric data with proper units. LOD/LOQ information should be reported separately from the analytical results. Some of the possible problems for consideration here are defining the terms and the difficulties in collecting this information. The definitions of LOD and LOQ can be slightly different depending upon the analytical method. Is the LOD/LOC by itself enough, or is other metadata necessary for complete understanding? Can we ask any reporter to describe both LOD and LOQ or are data accompanied only by LOD information acceptable?

Storing and reporting data outside of the LOD/LOQ
Data reported "below LOD" have little quantifiable meaning. These data should be reported as symbolic information specifying that the result was below the detection limit of the analytical method, not represented by "zero" or any other numeric surrogate. Quantification limits are generally reported with an upper and lower boundary. Data above the upper LOQ or below the lower LOQ are of limited accuracy and would also be candidates for some sort of symbolic rather than numeric representation. Analytical results larger than LOD, but less than LOQ could be represented numerically, however this should be a topic for discussion along with suitable metadata for LOD/LOQ values.

Discussion points for metadata items and structure
Information on analytical protocols
A description of the analytical protocols/methods for each analytical result is essential information for proper assessment of the monitoring data. Text-based descriptions of the method is one way of storing this information, however, more categorized or indexed approach to compiling analytical methods would allow searching and sorting of this information. Discussions in this area would include alternatives for storing and using this information.

Sampling site location
Sampling site location should be expressed by the harmonized way for geographical information system (GIS).

Information on the nature of sampling site
A comprehensive description of the sampling site characteristics is essential for proper use of monitoring data. A categorization system for the nature of the sampling site might be preferable to text-based descriptions. While text-based descriptions can provide a greater level of detail, categories, such as industrial area, urban area, background area, more readily lend themselves to searching indices in the later use of the database. The questions are (1) Should we use a categorization system, text-based description or both for describing monitoring sites? (2) If a categorization system is to be used, what types of site characteristics should be included in the database?

Sampling protocols
Sampling protocols are also essential information, especially when special sampling devices/methodologies are employed in the protocols. Information on sampling protocols could be collected separately, possibly using similar categorization and/or text-based information to analytical methods/protocols.

Information on QA/QC practices
Quality assurance and quality control (QA/QC) practices applied to monitoring data are important information when judging the quality of the data. Minimum requirement may be the yes/no information of such practices/programs on the data, however text-based information of the name of QA/QC programs and/or categorized information of the level of assurances/levels of controls/programs may be more valuable information.

Ownership of the data
Ownership should be established for all monitoring data included in the data warehouse. It is critical for users of the data to be able to contact the owner, if there are problems with the data or if additional information is required. An additional issue under this topic is ownership and/or intellectual property rights. This is a critical issue for a data warehouse containing data in individual databases. Topics for discussion here include, the level of detail required and practices for keeping ownership information current, ways to protect data that is not ready to be released, ways to release data that will minimize misuse.

Discussion items concerning presentation methodologies
Presentation and use of raw data
One issue that presents itself here is the choice of metadata to include in a download or display that makes the data most meaningful and less subject to abuse. Data gathered from a warehouse, which can include multiple individual databases, can be grouped, filtered, sorted and presented in ways that are inappropriate for the data or in ways that the owner of the data did not intend, if for example, the site characteristics or QA/QC information describing the numeric values are dismissed.

Presentation and use of summary data
Presentation of data in summary format (charts, graphs, statistical values, GIS) can offer insights into the meaning of data, but it can also over simplify and present an incorrect picture of what is truly happening in the environment. Are chemicals not being found in a certain location because the LOD is too high or because sufficient monitoring has not been conducted, or is contamination truly not there? By the same token, does the existence of many positive results in a particular area mean that it is more contaminated than other areas or that it is being monitored more efficiently? Topics for discussion in this area could include; effective presentation of the data, consideration of the nature of the data so that it is presented correctly, presentation of data outside of the LOD/LOQ values, inclusion of appropriate metadata, and data ownership issues.

Data exchange mechanisms and issues
The authors are working under the assumption that all data provided for this effectiveness assessment are to be made available to the public. With that assumption made, the Internet is by far the most convenient and least expensive way to share data

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with large numbers of people. Internet access to a data warehouse will provide the capability to share raw data, summarized data, and metadata on demand. It will also allow, through security measures, restricted access to certain parts of the data, if it is not ready to be released for any reason. Limited use of restricted access could be used to solve the intellectual property rights issues mentioned above under the Ownership heading.

The second issue under this heading is that all data collected for this effective assessment may not be electronically stored.   By definition a database is a collection of data without regard to the way that it is stored. Will the POPs data warehouse include non-electronic databases? If it does, how will the data be incorporated in to the warehouse so that its impact is not lost when the data are presented? Should there be periodic reports developed that include all data?

Some topics for discussion here might be the level of detail that will be provided (summary data only or raw data), the level of security that should be maintained on the Internet site (identification of users, different levels for summary information and raw data), the rights of data owners, appropriate inclusion of non-electronic data.

Strategies and approaches to developing data warehouse
Database structure in the data warehouse
The structure of the data warehouse will vary greatly depending upon its nature (centralized vs. distributed) and its size. If the warehouse is centralized, then designing table structures and relationships will be of primary concern. If the warehouse is distributed, the primary design focus will be an effective front end for accessing distributed data. If the data set is very large (millions of rows) a true data warehouse design may be the best approach. While these types of designs are often more difficult and time consuming, data mining and analytical capabilities can be greatly enhanced. If on the other hand, the warehouse will stay relatively small for some time a relational design may suffice. In either case the first step is determining which sets of data will be included and how they will relate to one another.

Data warehouse installation
Many countries already have databases for monitoring data, some of these are electronic and some are in paper format. We need to develop a strategy to best take advantage of all of the data in these databases. Topics for discussion here include: obtaining consistent/harmonized data elements from many different databases, moving and storing data from other databases while maintaining the original ownership, creating a data entry mechanism for non-electronic data. Manual data entry can be very costly, so we may wish to consider ways to include non-electronic data in summary reports without manually entering each value into a database.

Short-term and long-term strategies
A complete data warehouse is often hard to develop in a short period. Developing interim smaller products might allow user feedback so that the final product is more responsive to everyone's needs. Short-term and long-term strategies should be explored.

Development of example format of standardized database for warehouse
Reporting format to warehouse databases
Reporting format of the dioxin congener data are shown in Table 1 only as an example. Congener-specific analytical data is collected as numeric values with

specified unit information, with separate symbolic report for below LOD or below LOQ results. LOD and LOQ levels, procedural blank levels and recoveries of labeled standard are reported as numeric values. Analytical methods are referenced as an indexed reference of, in this example, Japanese official method compilation. Sampling site characteristics are reported as categories, and several additional pieces of information will be compiled (not shown in the example) as relevant metadata items. Although this is a reporting format and maybe too complicated, however, data items could be an example for the corresponding database structure.

Summary
Here will list the possible and necessary items that should be considered as the recommendation topics.

Recommendation for numeric data properties
- Analytical results with clear effective digit information.
- Unit for each data
- Distinction among below LOD, above/below LOQ and numeric values above LOD/LOQ
- Reporting for LOD/LOQ and above/below LOD/LOQ data

Recommendation for metadata items and structures
- Analytical protocols
- Nature of sampling site
- Sampling protocols
- LOD and LOQ
- Information on QA/QC practices
- Categorization system for metadata items if necessary
- Information on ownership and/or intellectual property rights
-

Recommendation for the presentation methodology of the data warehouse
- Data exchange mechanisms and issues
- Possible use of GIS for data presentation
- Internet presentation methodologies.
- Density of sampling points to get reliable averaging data

Strategies and approaches for building data warehouse
- How to take advantage of the databases that have already been built by some countries? In this case, how to get consistent/harmonized data items and properties?
- Is it better to develop new database in, for example, UNEP Chemicals? In this case, how to collect and develop new database respecting the ownership of the data?
- To identify short term and long term strategies

Table 1 : Data items and reporting format as an example. Dioxin congener-specific database is shown as an example.

Dioxin Congener Data Reporting Form (Provisional Image for Discussion)
(Taken from Japanese dioxin-monitoring database form at now in development at Ministry of the Environment)

Date of survey start		Owner of the data		
Date of surve finish		Analyzed by		
Prefecture		**T** Total (PCDDs+PCDFs)		(pg-TEQ / *)
City		**E** Total Co-PCB		(pg-TEQ / *)
location		**Q** Total (PCDDs+PCDFs+Co-PCB)		(pg-TEQ / *)
Location code or Water sample code		Longitude		
Sampling Site Characteristics***	Urban (code?	Latitude		
Media/Sample type	Perch	Method Reference	JIS K0301	
Specific characteristics	Muscle	Method description	HRGC/HRMS	
		Sampling Protocol	HVAS	

		Measured Conc. ** (pg / *)	LOQ (pg / *)	LOD (pg / *)	Recovery (%)	GC Column type
benzo-p-dioxi	1, 3, 6, 8-TeCDD					4 to 6 Cl cong.
	1, 3, 7, 9-TeCDD					
	2, 3, 7, 8-TeCDD					□ SP-2331
	1, 2, 3, 7, 8-PeCDD					□ DB-17
	1, 2, 3, 4, 7, 8-HxCDD					□ CP-Sil88
	1, 2, 3, 6, 7, 8-HxCDD					□
	1, 2, 3, 7, 8, 9-HxCDD					□
	1, 2, 3, 4, 6, 7, 8-HpCDD					
	OCDD					
Dibenzofurans	1, 2, 7, 8-TeCDF					
	2, 3, 7, 8-TeCDF					7, 8 Cl cong.
	1, 2, 3, 7, 8-PeCDF					□ DB-17
	2, 3, 4, 7, 8-PeCDF					□ HP-5
	1, 2, 3, 4, 7, 8-HxCDF					□ SP-2331
	1, 2, 3, 6, 7, 8-HxCDF					□ CP-Sil88
	1, 2, 3, 7, 8, 9-HxCDF					□
	2, 3, 4, 6, 7, 8-HxCDF					□
	1, 2, 3, 4, 6, 7, 8-HpCDF					
	1, 2, 3, 4, 7, 8, 9-HpCDF					
	OCDF					
Coplanr PCBs — Non Ortho	3, 4, 4', 5-TeCB (#81)					PCB cong.
	3, 3', 4, 4'-TeCB (#77)					□ DB-5MS
	3, 3', 4, 4', 5-PeCB (#126)					□ HT-8
	3, 3', 4, 4', 5, 5'-HxCB (#169)					□
Coplanr PCBs — Mono Ortho	2', 3, 4, 4', 5-PeCB (#123)					□
	2, 3', 4, 4', 5-PeCB (#118)					
	2, 3, 3', 4, 4'-PeCB (#105)					
	2, 3, 4, 4', 5-PeCB (#114)					
	2, 3', 4, 4', 5, 5'-HxCB (#167)					
	2, 3, 3', 4, 4', 5-HxCB (#156)					
	2, 3, 3', 4, 4', 5'-HxCB (#157)					
	2, 3, 3', 4, 4', 5, 5'-HpCB (#189)					
DD Total	TeCDDs		-	-	-	-
	PeCDDs		-	-	-	-
	HxCDDs		-	-	-	-
	HpCDDs		-	-	-	-
	OCDD		-	-	-	-
	Total (PCDDs)		-	-	-	-
DF Total	TeCDFs		-	-	-	-
	PeCDFs		-	-	-	-
	HxCDFs		-	-	-	-
	HpCDFs		-	-	-	-
	OCDF		-	-	-	-
	Total (PCDFs)		-	-	-	-
Total (PCDDs+PCDFs)			-	-	-	-
Total Co-PCB						
Total (PCDDs+PCDFs+Co-PCB)			-	-	-	-

*) Liter, m3 or gram (dry, wet or lipid)
**) "ND" or "NQ" should be reported instead of numeric values if it is the case
Reporting format for data between LOD and LOQ is not defined now
***) Examples are : Urban, Industrial, Residential, Background, Around sources, etc.

Assessment of Global Capacity Building

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Abstract

Given the wide disparity in economic and technical development between countries, the development of capacity to undertake monitoring of POPs should be geared to avoid overlap and inefficiencies. This entails that technology transfer between developed and developing countries should be done regionally with countries having common language, shared environmental concerns and existing relevant multi-lateral agreements continuing to work together to establish data on POPs. In order to achieve a global dimension, it would be useful if all countries that have signed under the Stockholm Convention make commitment to work together under a Global Monitoring Programme that recognises and aids these regional programmes, initiate others where necessary and provide leadership in establishing unified direction for sampling, analytical techniques, reporting protocols, information exchange and a global database. At all stages, this is best achieved by building on existing initiatives. It would be prudent to begin a programme to establish compatibility among the developed nations with capacity building in the developing countries following the pattern set toward achieving global harmonisation for monitoring POPs.

Introduction

The capacity and needs to manage POPs across countries is varied and differs markedly depending on the overall level of development of the countries in particular and the various regions on a whole. In order to make a meaningful assessment, regions are categorised and addressed based on the relative levels of development. Three categories are presented: Category I includes North America and Europe and represent, in the main, only developed countries. Category II includes the Mediterranean, Central and North East Asia along with South East Asia and South Pacific. Category III includes Sub-Saharan Africa, the Indian Ocean, the Pacific islands, Central America and the Caribbean and also Eastern and Western South America. While the assessment will introduce sample situations from countries within these categories, emphasis will be placed on alternatives for technology transfer and capacity development.

Monitoring Capacity

Given the key role that monitoring will play in the control of POPs, it is instructive that global and regional and national programmes be developed to undertake monitoring of POPs throughout all compartments of the environment. Such development should include:

♦ Updating of equipment and analytical techniques, especially for industrial and unintentionally produced POPs.

♦ Setting up national and regional reference laboratories. Strengthening regional laboratories both in terms of capability and capacity to provide analytical services to countries where size and demand for testing does not justify developing national laboratories.

♦ Supporting the upgrading of existing laboratories on QA/QC and accreditation processes.

♦ Increasing the budget for carrying out analyses of POPs.

On a global scale, there is not much monitoring of POPs being done on a consistent basis. Most analyses of POPs are done at the research level by academic institutions mainly for scientific interest and also to satisfy the study of particular environmental accidents that occur ad hoc. However, much effort has been made with limited resources in some developing countries. At all times, assessment should be made of ongoing work and new initiatives to increase monitoring capacity should be built on these efforts. In order to provide a perspective of the monitoring programmes globally, examples are presented from the regions based on the categories outlined above.

Category I Regions

While the capacity to monitor POPs in North America and Europe is advanced compared to other regions, there is still a strain to provide the necessary resources to analyse the ever-increasing number of chemicals being produced and used.

North America

Canada, the USA and Mexico provide a good example of regional cooperation in establishing inventories of releases of substances from facilities and other sources to the environment. In particular, Canada maintains its National Pollutant Release Inventory (NPRI) and the United States its Toxics Release Inventory (TRI). These programmes mandate by law that all facilities and industries report data annually on

releases and transfers of selected chemicals to the environment. The NPRI reports on some 300 chemicals while the TRI includes over 700 chemicals. Both programmes contain POPs chemicals.

Along with Mexico, Canada and the United States have joined to establish the tri-national Sound Management of Chemicals (SMOC) programme. This programme collects through Pollutant Release and Transfer Registers (PRTRs), information on chemicals including POPs in order to establish North American Regional Action Plans (NARAPs). This regional effort has allowed the update of inventory for releases of dioxin and dioxin-like compounds across all three countries. Much of the success of these programmes in North America are attributable to the cooperation between industry and government regulatory institutions. Transparency is agreed where information may affect the public at large but other sensitive data considered confidential for other competitors is kept as such.

In terms of environmental monitoring, both Canada and the United States have established extensive programmes for checking certain key environment areas. Canada has a broad based scientific partnership among stakeholders from all sectors. The Ecological Monitoring and assessment network (EMAN) brings together individual monitoring activities to prioritise the contaminants that are affecting various ecosystems. The International Joint Commission have been monitoring cross-border areas such as the Great lakes ecosystem and the U.S. EPA is carrying out a study on Fish Tissue to research the levels of persistent bio accumulative toxic chemicals in fish (North America Regional Report, 2002).

These and other initiatives in monitoring long range transport of selected POPs allows Canada and the United States to keep abreast of certain chemicals that have shown to represent possible danger to the environment of these countries. Even so, the programmes are usually a response to particular problems and are not necessarily ongoing programmes on a general basis. Also, given the economic links created between Canada, the United States and Mexico, there are still only limited monitoring capabilities and exercises being undertaken in Mexico. The efforts of the SMOC initiative in developing NARAPs go a long way in ensuring monitoring of selected substances in this region and demonstrate the usefulness of regional collaboration in tackling the problem of POPs especially considering the transboundary movement of these chemicals. However, even in this more developed region of the globe, funding is still inadequate particularly in Mexico where resources are far less than in Canada and the United States.

Europe

Within the Europe Region, there are many monitoring programmes that have been used successfully to maintain control of the releases and deposition of POPs especially in major water bodies. A list of these is captured in Table 5.1. Besides these elaborate regional programmes, many countries in Europe conduct extensive national monitoring programmes in various scope and intentions. However, similar to the case of Mexico in the North America region, many countries in Eastern Europe including Moldova, Belarus and the Ukraine have no ambient air measurements and limited information concerning other environmental compartments (Europe Report 2002).

Table 5.1   Ongoing monitoring programmes for POPs in the Europe region

Global Environment Monitoring System – Food Contamination Monitoring and Assessment Programme EURO (GEMS/Food-EURO)	Monitoring of contaminants in food and assessment of contribution to human exposure and significance to public health and trade
The Co-operative Programme for Monitoring and Evaluation of the Long range Transmission of Air Pollutants in Europe	Monitors the movement of pollutants in the atmosphere across State boundaries and in and out of the region
The Convention on the Protection of the Marine Environment of the Baltic Sea Area (HELCOM)	Monitors the level of pollutants in the Baltic marine environment
The Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR)	POPs are measured in the Arctic Waters, the Great North Sea, the Celtic Seas, the Bay of Biscay, the Iberian Coast and the Wider Atlantic
The Caspian Environment Programme (CEP)	Monitors the condition of the Caspian Sea

Category II Regions
In these regions, the disparity in monitoring exercise is wide between countries and the conditions for collaboration are not as easy given the differences in language, culture and capacities that exist. International waters has played however, a catalytic role in bringing together countries of varying development that have a water body as a common border. More and more, this pathway to collaboration is being used to create conventions, agreements and bonding between countries as it is in the interest of all to ensure the protection of bordering water bodies. This is even more critical when considering fresh water, as this is a dwindling resource worldwide.

The Mediterranean
The three more developed countries of the Mediterranean – France, Italy and Spain – combined have established over 10 distinct monitoring programmes covering all compartments of the environment. This is in sharp contrast to the countries south of the Mediterranean. Most have just limited monitoring activities with Lebanon, FYR Macedonia, FR Yugoslavia showing no programmes for monitoring persistent toxic organic pollutants.
Still, in response to the increasing pollution of the Mediterranean Sea, the Mediterranean Pollution Monitoring and Research Programme was formed in 1975. Its main aim then was the establishment of a network of institutions undertaking marine pollution work and the collection of information regarding the level of pollution in the Mediterranean Sea. The monitoring activities covered heavy metals in marine biota (mainly mercury and cadmium), halogenated hydrocarbons in marine biota (mainly PCBs and DDTs), and petroleum hydrocarbons in seawater. The development and maintenance of these national monitoring programmes was the aim of the second phase (1981), whereas more recently (1996), the emphasis shifted from pollution assessment to pollution control (Mediterranean Regional Report, 2002).
In this latter phase, the introduction of quality control and common reference methods for the analysis of contaminants in the various matrices has definitely been the most important achievement of the MEDPOL Programme. The use of certified reference

materials and common analytical methods provided a good approach to the collection of meaningful data and allowed their comparison on a Mediterranean-wide scale. In total, 17 laboratories across countries of the Mediterranean take part in delivering comparable data on selected substances. The revised programme has allowed for considerable improvement with time in the number of analytes measured and the reduction in technical errors being made.

The MEDPOL programme underwent a massive capacity building exercise during the first 15 years. Many scientists were trained, laboratories equipped with suitable up-to-date equipment, consultants were hired to provide advice, workshops were organised, analytical methods were corroborated and intercalibration exercises carried out between laboratories. Even though mistakes have been made and there are some areas that still need to be improved, the MEDPOL initiative represents an example of achievement among countries with a common desire to protect a valuable resource from chemical pollution.

Central and North East Asia

In this region, there are four countries that undertake national monitoring programmes on POPs. These include: Japan, China, South Korea and the Russian Federation. There are no monitoring exercises done in the other eight countries. Even within the top four countries, only Japan has established a comprehensive programme that covers most POPs. There, the Ministry of Environment has an elaborate structure of scientists and other personnel dedicated to carrying out monitoring of differing compartments of the environment. Environmental monitoring started from 1974 and Japan has been reporting monitoring data annually in *Chemicals in the Environment* (or KUROHON—"black book" in Japanese). The monitoring includes several categories: 1) a survey of prioritised chemicals (c.a. 20 compounds each year) in air and water; 2) yearly monitoring by GC/MS of Class I and frequently detected chemicals in water and sediments; 3) yearly GC/ECD and GC/FPD monitoring of Class I organochlorines and organotins respectively in mussels and other organisms; 4) monitoring of residue levels of some of the designated/registered chemicals in ambient air, indoor air, foods, water and sediments; 5) monitoring of unintentionally produced chemicals (until 1997 - PCDD/PCDF and coplanar-PCBs; 1998 - PBDDs and PBDFs).

Even though effort has been made to set up systems in the other advanced countries, there is still a major void for monitoring POPs specifically. A link has been made between Japan and South Korea to carry out a joint research program to study EDCs such as PCDD/PCDF and PCBs. Research includes methods to monitor and techniques to test EDCs. Organisations taking part in the program include NIES of Japan and NIER of South Korea (Central and North East Asia Regional Report, 2002).

Given its position of strength technically, Japan offers a good opportunity for collaborative work to monitor the Sea of Okhotsk (Russian Federation), the Sea of Japan (South Korea/Russian Federation), the Yellow Sea (China/South Korea) as well as initiating pre-emptively, monitoring of reverine flows into these major marine water bodies from the Amur, the Huang He (Yellow River) and the Chang Jiang (Yangtze River).

Most of the other countries in this region are landlocked and so do not offer much incentive for collaboration in terms of water bodies. However, Mongolia and the Russian Federation share the Celenge River that empties into the Baikal Lake and the Kerulen River transects both Mongolia and China. As rivers pose a major opportunity

for the transboundary pathway for pollutants attached to sediments, the monitor of other smaller rivers that course between States can also be included in joint control exercises for pollutants.

South East Asia and Pacific

Even though Australia and New Zealand have superior monitoring capabilities, some of the other countries in this region are making great strides in instituting programmes to check on releases to air, water and land for some of the POPs being assessed. New Zealand and Australia have now established the capability to analyse for PCDD/PCDFs and this capability is being instituted in Malaysia, Thailand and Singapore (Region 8 Report, 2002). All these countries are already doing some monitoring of organochlorines but there is still no regional coordinated programme to look at these substances.

Category III Regions

With the exception of India, all the countries within these regions lack comprehensive monitoring programmes. Most do ad hoc testing of organochlorines based on research, perceived hotspots or for filling legal requirements. Industrial facilities in these countries may undertake routine analyses of effluents and emissions but such data is considered confidential and rarely is presented for public scrutiny.

There is little doubt that the lack of financial resources is the key disincentive for creating monitoring programmes for POPs. Unless controlled, regional programmes are developed with full long term support from the developed countries, it is unlikely that data will be available over extended periods from these countries. Given the movement of these persistent chemicals through air and possibly attached to sediment in reverine flow, it is to the benefit of all that such collaborative programmes are instituted in these developing regions.

Existing Regulation And Management Structures

The level of monitoring of POPs is concomitant with the degree of regulations and infrastructure established in the various regions. Financial wealth invariably dictates the magnitude of the regulatory structures being employed to control chemical contamination of the environment.

Category I Regions

Between North America and Europe, there are many sophisticated regulatory systems and structures for controlling chemicals. These systems underscore the financial wealth available from the development of the private industry but also the subsequent need to provide a controlling balance to the ever-increasing levels of input and output of chemicals from these industries. The study of Lake Michigan under the Integrated Atmospheric Deposition Network - a cooperative link between Canada and the United States – to study the complex pathways of POPs (PCBs, atrazine, trans-nonachlor and mercury) provides a successful example of this regulatory function.

The complex web of regulatory systems for these regions are approached either in a diverse or central direction from country to country. Canada has nine different pieces of federal legislation covering the control of POPs. The approaches include the intent for i) virtual elimination, ii) management of substances during their life cycle, iii) voluntary regulation.

The United States has a more centralised system where the Environment Protection Agency (EPA) oversees all matters pertaining to protection of human health and the

integrity of the environment. EPA also uses a broad range of approaches to manage POPs including regulatory, compliance assistance, enforcement, research, voluntary actions and international negotiations. In so doing, the United States has the widest experience in regulation of POPs and along with other developed systems, presents the best opportunity for providing assistance in the development of regulatory mechanisms in developing countries (North America Regional Report, 2002).
On the other hand, Mexico, like Canada, has several pieces of legislation through which POPs are regulated. However, the difference is that there is multi-overlap between these legislation and eventually much confusion as to who is doing what. Still, with the assistance from its NAFTA partners, Mexico has been improving its regulatory system and is steadily bringing itself in line with the elaborate processes established to the North.

Category II Regions
Again, the disparity in regulatory mechanisms between countries in these regions is evident. Countries such as Japan, Australia, France and Italy have extensive regulatory organisations that control all aspects of POPs including, monitoring of emissions, standards for environmental levels, management of accidents, voluntary and mandatory reduction programmes and regulatory framework for storage and disposal of these chemicals.
In Central and North East Asia, Japan, has specific laws pertaining to POPs (see Table 5.2). This provides a clear message on the importance placed on the concern given to POPs by the Japanese government and allows for control of the release of these chemicals to the environment.

Table 5.2   Major laws concerning regulation of POPs in Japan

Japan	Law Concerning the Examination and Regulation of Manufactures, etc. of Chemical Substances (1973)
	Agriculture Chemicals Regulation Law (1948)
	Law Concerning Special Measures against Dioxins (1999)
	Law for the Promotion of Environmentally Sound Destruction of PCB Waste (2001)
	Law Concerning Reporting, etc. of Release to the Environment of Specific Chemical Substances and Promoting Improvements in their Management (2001)

Source: Taken from the Central and North East Asia Regional Report, 2002

Where many other countries also have enacted laws and have environmental standards, Japan ensures that there is compliance and these laws and standards are enforced.
A similar picture is gleaned from the Mediterranean region for France and Italy. Here, these countries like others in Europe, are covered by their association to the European Commission (EC). There are many EC directives pertaining to POPs and countries within this regional economic integration organisation are obliged to enforce these measures. The general strategy of the EU to address environmental issues of chemicals is part of the general objective of the Sustainable Development taking place while considering the potential responsibilities of the chemical industry in relation to the precautionary principle. Some Directives relevant for the regional POPs strategy are:

Directive 2000/76/EEC on waste incineration.

Defines limit values on emissions of particles and total organic matter from incineration of all type of wastes. Substances addressed are, e.g., PAHs, PCDD/PCDFs and mercury.

Council Directive 2000/60/EC of the European Parliament and of the council establishing a framework for Community action in the field of water policy (Water Framework Directive).

This Directive contains provisions on measures aimed at progressively reducing (for priority substances) and at ceasing or phasing out (for priority hazardous substances, within 20 years) discharges, emissions and losses as well as identification of these priority substances and hazardous priority substances (emission inventories according to Article 13(4)). The EC has two years to propose control measures necessary to reach the objectives for priority (hazardous) substances. These substances will have to be monitored as mandatory parameters under the WFD.

Council Directive 86/280/EEC on limit values and quality objectives for discharges of certain dangerous substances included in List I of the Annex to Directive 76/464/EEC (Council Directive 76/464/EEC of 4 May 1976 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community).

This Directive limit values for emission standards for the substances referred to in Article 2 in discharges from industrial plants, quality objectives in the aquatic environment, time limits for compliance, reference methods of measurement. It establishes a monitoring procedure, requires Member States to co-operate and to draw up programmes to avoid or eliminate pollution arising from the sources referred to in Article 5. The Directive applies to the waters referred to in Article 1 of Directive 76/464/EEC, with the exception of ground water. Substances addressed are: DDT, the drins, PCP, hexachlorobenzene.

Council Directive 96/61/EC concerning integrated pollution prevention and control (IPPC).

The objective is to prevent or minimise air, water and soil pollution by emissions from industrial installations in the Community, in view of achieving a high level of environmental protection. This Directive requires the assessment of chemicals used in certain production processes and certain conditions for the licensing of industrial installations. Article 15 (3) of the Directive requires Member States to inventory and supply data on principal emissions and responsible sources, that is from all large facilities with one or more activities as mentioned in Annex I to this Directive. According to this Article 15 the Commission decided on the implementation of an European Pollutant Emission Register (EPER). Substances addressed include PCP, HCB, HCHs, PCDD/PCDFs and organotin compounds (Mediterranean Regional Report, 2002).

In South East Asia and South Pacific, Australia has established regulatory schemes to manage POPs. In 1975, Australia established the National Environment Protection Council (NEPC) to enable the development and implementation of a consistent and national environmental protection policy through the development of national environment protection measures. As at June 1998, NEPC had made measures for the National Pollutant Inventory (a Pollutant Release Register), the Movement of Controlled Waste across State and Territory borders and Air Quality Standards (National Chemicals Profiles, 2000).

In marked contrast, the developing countries in all three regions have limited legislation to deal with POPs. Where legislation does exist, the full complement of personnel and adequate equipment and infrastructure to implement and enforce are not in place. A typical example is the status of Mongolia in Central and North East

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Asia. In outlining their chemical management programmes, Mongolia refers to
expectations as currently, there is little management being implemented. The goals of
Mongolia include:

- Assessment and Classification of Dangers Entailed by the Use of Chemical
  Substances and Products

- Create a risk assessment system for chemical substances consistent with
  international standards;

- Reduction of Dangers from Toxic Chemicals and Creation of an Information
  Exchange System

- Reduce substantially chemical hazards in all aspects of its "life cycle";

- Create systems that promote information exchange with other countries and
  international organizations on chemical security, hazards and waste.

- Strengthening the Chemical Management Capacity

- To create a national system for proper utilization and reduction of toxic chemicals
  ensuring the ecologically safe system, developing and implementing essential
  norms and standards (Central and North East Asia Regional Report, 2002).

These are worthwhile objectives for any country. Unfortunately, it is doubtful that
without financial and technical assistance will Mongolia be able to achieve its goals
for chemical management. A similar situation exists for the other developing
countries in that region.

In the Mediterranean, pesticide control is mainly carried out by a system of national
registration, which limits the manufacture and/or sale of pesticide products to those
that have been approved. Most developing countries have limited capability to carry
out their own tests on pesticides and tend to adopt regulatory criteria from the
developed world. Some of these countries, like Egypt, Morocco, Tunisia, Syria,
Cyprus and Turkey have their own Pesticide Registration offices that handle the
management of pesticides. Although many of them have developed the regulation of
industrial POPs, they do not usually have the management capabilities in place to
carry out monitoring exercises.

Some of the developing countries of South East Asia and South Pacific have been
making strides in instituting regulatory mechanisms to deal with POPs. Besides
having a wide array of laws to manage POPs, Thailand has obtained assistance in
carrying out PCDD/PCDFs emission level inventories and is establishing a laboratory
to undertake these analyses. Most developing countries within this region have
legislated laws to regulate chemical substances. The major drawback is the state of
enforcement of these laws given the inadequate number of qualified personnel and the
poorly equipped laboratories assigned to implement enforcement.

Category III Regions

The countries in Sub-Saharan Africa, the Indian Ocean, the Pacific Islands, Central America and the Caribbean and Eastern and Western South America all undertake limited monitoring of POPs. Most carry out analytical surveys designed to answer a specific question for research or to investigate a particular problem that has been found pertaining to a specific chemical. It is evident from available data that most of the countries of the region have developed, and others are in the process of developing policies and regulations in the management of chemicals including POPs. It is possible that the low level of awareness among the stakeholders and the poor dissemination of available information of the adverse effects of POPs on humans and the environment, are responsible for the slow pace in developing regulations and policies on POPs. Even then, some of the existing national policies need to be reviewed in response to new challenges and international obligations within existing Conventions (e.g. Stockholm Convention on POPs).

It is also evident that most countries have established or are developing institutions to manage the environment but lack management strategies regarding hazardous chemicals. There is further evidence that these institutions also lack adequate capacity and resources for the environmentally sound management of hazardous chemicals and POPs. A major constraint towards sustainable chemical management is the lack of and/or weak enforcement of regulations. For these regions to contribute effectively in the global effort to monitor POPs, there is need to establish and/or strengthen existing institutions and legal frameworks through capacity building and putting in place necessary mechanisms for compliance monitoring and enforcement.

Sub Saharan Africa

There are no regional programmes documented for the regulation and control of POPs. There are individual country programmes including the inventory of pesticides being carried out by the World Bank and FAO and the DDT elimination initiative for certain countries. However, the general awareness of these substances is low and given the perceived greater needs of these countries, such regulatory development is low in priority.

Indian Ocean

The activities undertaken in the region by the UNEP/Regional Organisation of the West Asia (ROWA) can be summarised under the following headings:

- Promote Multi Lateral Environmental Agreements (MEA's)

- Help in developing/implementing NIPs

- Provide capacity building activities and pilot projects in cooperation with CAMRE and Convention Secretariats by backstopping support from UNEP Head Quarters out posted offices

The Regional Organization for the Protection of the Marine Environmental (ROPME) came into existence after the 1978 Regional Conference on the Protection and Development of the Marine Environment and the coastal Areas of Bahrain, I.R. Iran, Iraq, Kuwait, Oman, Qatar, Saudi Arabia and United Arab Emirates. Since its establishment, ROPME has provided technical coordination and assisted its eight member States in the implementation of a number of projects on environmental monitoring and management (Indian Ocean Regional Report, 2002)

While most of the countries in this region have laws pertaining to pesticides, there is little control of industrial chemicals. No country has regulations governing the emissions of dioxins and furans nor the capability to analyse such emissions.

The Pacific Islands

Most countries in the Region have regulations covering imports and use of pesticide POPs. However, all other POPs chemicals are mostly not controlled or in many cases partly covered by regulations for other related areas such as Public health and Environment Acts. Also there is a general lack of the management and administrative structures needed for proper control and enforcement of existing regulations. The French and US territories are generally better off through the regulations, support and controls provided by the "parent" states (Pacific Islands Regional Report, 2002).

Central America and the Caribbean

It is evident that basic legislation exists for the implementation and adequate control of pesticide management in the Region, but there is space for improvement and for harmonization, as has already been done by some Central American countries.

In some countries such as Barbados, Cuba, Jamaica and Colombia, there are specific regulations for a reduced number of industrial POPs. The regulations are general, and few allow an effective management of POPs and adequate enforcement. The situation is worse in relation with emission of dioxin and furans. Only Jamaica reports national regulation of dioxin and furan emissions to be implemented in 2004. Costa Rica is developing sample procedures and analytical methods for POPs emissions (dioxins and furans), however, at the moment there is no regulation of these compounds (Central America and the Caribbean Regional Report, 2002).

Eastern and Western South America

Brasil is the only country with capability to analyse PCDD/PCDFs. However, the control of industrial chemicals in general is ad hoc and dependent on the area of the country being considered. All countries within this region have regulations to control pesticides and chemicals in general. However, the infrastructure to carry out these laws is not competent enough to ensure meaningful monitoring.

Polar Regions

As there are no inhabitants permanently at the Antarctic, there are no regulations specifically for controlling certain human activities. Environmental protection within the Antarctic Treaty area is governed by a protocol to the treaty.   This protocol states that 'activities in the Antarctic Treaty area shall be planned and conducted so as to limit adverse impacts on the Antarctic environment and dependent and associated ecosystems'(Antarctica Regional Report, 2002).

In the Arctic, regulations are covered within the countries responsible for the respective section of the region. The Nordic Council of Ministers has proposed guidelines for POPs concentrations in food. Although covering only a restricted segment of the circumpolar Arctic (between longitudes 44° W and 51° E), the 1992 Convention for the Protection of the Marine Environment of the North East Atlantic (OSPAR), is currently one of the most applicable international agreements addressing Arctic marine pollution from various sources. On both monitoring and source-related assessment issues, therefore, OSPAR 1992 represents a relevant agreement to be taken into account (Arctic Regional Report, 2002).

The monitoring of POPs levels in the environment varies from country to country depending on the level of development and financial resources available. The few

established organizations and research institutions that exist in developing countries, lack adequate trained scientists and proper equipment to monitor and assess POPs in various media. Data that might have been generated by research is rarely published and disseminated to relevant authorities that might use such data to establish control measures or perform enforcement. It must also be noted that most generated data, if not all, are from individual studies, and not ongoing. This has resulted in fragmentary data and numerous data gaps. Despite these limitations, the increasing awareness about POPs is stimulating cooperation amongst the various research institutions and other stakeholders. This may be a good indication of proper future POPs management in these regions.

Status Of Enforcement

The status of enforcement takes a similar line to the pattern of regulations and laws in the various regions. In North America, the United States of America has a set of regulations covering over 900 pages. All of these regulations are enforced in some way resulting in a comprehensive programme ranging from the control of the chemical industry, the analysis of emissions and releases, the monitoring of environmental compartments, to the handling of hazardous chemical waste. Along with this set of programmes, there is a constant promotion of awareness of the dangers of POPs, especially through an array of non-governmental organisations that provide public involvement and a non-tolerant approach to matters concerning human health and the integrity of the environment. Even so, the vast number of production sites that have chemicals as inputs or outputs, make it difficult to maintain control of the possible emissions that can occur.

On the other hand, many developing countries in Sub-Saharan Africa, the Mediterranean, the Indian Ocean, Central America and the Caribbean, Central and North East Asia and South East Asia and South Pacific have laws and regulations but cannot enforce them. States facing low levels of organisational capacity and weak economies have serious difficulties in increasing environmental protection and fulfilling international commitments. In this respect, investigations have shown that old stocks of chlorinated pesticides (e.g. lindane) continue to be used in practice under no control of the authorities and that even banned products such as DDT are still being illegally imported in some of these countries. In Sub-Saharan Africa, no country has policies to address POPs specifically and only approximately one half have the proper institutional framework to implement any such policies.

However, there are examples where developing countries, with some assistance have made strides in controlling the emission or release of pesticide POPs to the environment. In Jamaica, the German aid agency GTZ provided financial assistance for developing the Pesticides Control Authority (PCA). This institution is legislated to regulate the pesticides industry in Jamaica but no implementation of the legislation was undertaken for eighteen years after enactment. The key feature that caused sustained success of the development of the PCA was that the legislation allowed the PCA to collect and spend its revenue stream solely on areas for controlling pesticides. Revenue was gained from charging a percentage of value of chemicals imported into the country along with other fees for registration etc. Besides instituting and enforcing regulatory mechanisms without strain on the central purse, the PCA was able to undertake systematic analytical surveys of water, foodstuff and pesticide products (Hyacinth Chin Sue, 2003).

There are no satisfactory regulatory or management strategies in place for POPs of industrial uses such as HCB and PCBs in the Indian Ocean region countries. Even enforcement of the regulations in existence has been poor.

In the case of POPs of unintended by-products, no regulatory or management control measures are in place except the establishment of standards for levels in environmental compartments by a few countries in the region.   It is difficult to see extensive improvement in the enforcement of POPs in most of the developing countries in the medium term. There are implementation plans being developed for countries that have signed the Stockholm Convention. However, logistics for actually implementing these plans is not yet finalised.

Technology Transfer

The transfer of technology to facilitate monitoring of POPs in sources, environmental concentrations and eventually the effects, requires the involvement of all stakeholders between countries and a willingness for the donor and receiving parties to understand the limitations to be addressed. Technology is not always appropriate. Introduction of improved technology has, on many occasions, failed because the culture, climatology, laws and inadequate infrastructure to support viability have not been considered during transfer. Some of the avenues of transfer are discussed below with consideration to where breakdown may occur.

> **Scientific Workshops** – This tried and tested method of information exchange continues to create a medium for participants to meet and exchange views and ideas. Besides showcasing innovative concepts, such fora initiate contacts and create friendships that go a long way toward generating collaborative efforts for technology transfer.

> **The Internet** – Now an accepted form of gaining information, the internet is increasingly becoming the primary source for all facets of the society to seek information. Especially among students, the internet is accepted as the place to display new technology to capture the largest audience possible. As more of the populous within developing countries tack on to the internet library, this means of data exchange will be a vital link to these countries in the quest to keep pace with sampling and analytical methods for POPs and other pollutants. However, there is still need for structuring this vast network to ensure that quality can be a function within the search exercise.

> **Multilateral Environmental Agreements (MEAs)** – Such agreements have served as a platform for technology to be transferred between parties to any given agreement. Good examples include the Montreal Protocol on protection of the Ozone layer and the Stockholm Convention on the reduction of POPs. On the regional scale, these MEAs have been even more influential and should be encouraged especially where a common bond is available. The linkage between countries that share a common water body is a suitable example. The MEDPOL organisation in the Mediterranean, the CEC in North America and the EMEP research in Europe are typical examples. Even if such agreements exist and are working well, it would be suitable for countries that have signed to the Stockholm Convention to also agree to participate in this global exercise to allow central control of global monitoring. Then, the chances of exacting greater efficiency and avoidance of overlap are increased considerably.

Adoption of Countries – The adoption principle for growth and development has been used in other spheres of life. Cities and universities in different countries have used this link to great advantage over the years. In this instance, it requires the linkage between a developed country and one or more developing countries in a particular region to work together toward the improvement of technological practices in the developing country. In some instances, the developed countries can also benefit from exposure to the indigenous practices of the developing country that has potential on a wider scale. This alliance can allow the exchange of personnel for training in both directions, the increase in the understanding of the culture between countries and the timely improvement of the environment as the process is expected to continue over an extended period. Commitment from both sides is the key factor in such a process. It is suggested that countries from both levels of development be invited to participate in a global scheme. Common threads are sought to link countries together. Such bonds include:

Language – A vital means of communication that goes a long way toward having harmonious relations between countries. Developing countries would seek to form alliances with those countries sharing the same language to allow for easy transfer of technology, training and scientific workshops.

Regional Pairings – If both parties have a common environmental concern, it will be a useful incentive for collaboration. This represents the best opportunity for success globally and investigation should begin to review current collaboration and how best to foster new links on a similar basis where none now exist.

Shared Responsibilities – The collaboration that is to be developed must also intertwine between developing countries within a region. It is foolhardy for neighbouring developing countries to seek to create the expertise in the same expensive non-sustainable analytical technology. Therefore, there must be an overall strategy where countries that have signed on to the programme accept the responsibility to provide certain services for others in the region and for the reciprocal undertaking to be acceptable for other capabilities. Additionally, it must be understood that trained personnel should remain within his/her State for a given period to ensure development of a cadre of experts. Too often, persons trained leave for the developed countries having been lured by attractive offers.

Use of Existing Collaborations – There is no need to 're-invent the wheel'. There are many regional monitoring programmes that already exist and are productive. These should be logged and an analysis done to see how best to integrate these programmes into a global exercise. The developed countries of North America, Europe, East Asia and South East Asia should immediately seek to increase the pace toward compatibility of analytical methods, quality assurance and data presentation. Here is the key to future development of global monitoring. If the same analytical language is spoken at this level, the stage will be set for compatibility to trickle down to the other countries around the globe.

Conclusions

The protection of the environment and human health from the adverse effects of POPs chemicals requires significant monitoring capacity worldwide that are effectively integrated and coordinated within countries but also between countries within a given region. This coordination has to extend to a global level.

Adequate capacity is required in:

- Laboratory capability for monitoring and testing of sources, environmental and product contamination and human exposure

- National, Regional and International Legislation including laws to monitor sources, environmental concentrations, effects and disposal of POPs

- Human resources for training, sampling, analyses and data compilation and assessment.

Within the developed countries, there is monitoring ongoing for POPs. Even so, the financial pressure to keep abreast of the required analyses for the increasing number of chemicals is daunting. In North America, the links forged between the United States of America, Canada and Mexico have brought positive results for all three countries as work is shared, information is exchanged and assistance has been given to Mexico to bridge the gap in capability. The SMOC programme carried out by the CEC has allowed focus on particular POPs that are priority for that region.

For Europe, the EC has created policies that make it mandatory for member countries to have monitoring programmes for selected chemicals. However, the many countries outside of the EC in this region are still saddled with stockpiles of PCBs, obsolete pesticides and relatively high emissions of PCDD/PCDFs from inefficient industrial plants. These countries mainly from Eastern Europe will probably benefit upon accession to the EC where strict policies will have to be accepted and enforced.

The creation of the MEDPOL initiative in the Mediterranean can be argued as a success story for collaboration between developed countries and others sharing a common environment body open to pollution from poor protective directives. The programme is not perfect but has been used to establish legislation, improve human resources, develop laboratory capability, create monitoring exercises, increase meaningful enforcement and institute preventive and corrective measures especially in the developing countries to the south of the Mediterranean Sea. Much can be gleaned from this initiative and other regions should consider studying the programme with a view to possibly imitating at least the concept behind the programme.

In Central and North East Asia and South East Asia and South Pacific, there is limited regional collaboration taking place on the monitoring and control of POPs. These regions are not grouped by any common water body and this may be the missing link required to bring them together on POPs problems. Japan to the north and Australia and New Zealand to the south are advanced in PCDD/PCDFs analyses for emissions to air and even though some of the countries around these two have made effort to increase capability, many others are still lacking. It requires novel and innovative ways to transfer technology and information to these lesser developed countries as many of the high profile initiatives will not be sustainable there.

In Sub-Saharan Africa and Central America and the Caribbean, two projects recently created should have telling effect on the reduction of pollution to the environment. The African Stockpile Reduction Programme and the Pesticide Runoff Reduction to the Caribbean Sea programme will both have major impacts in protecting the environment of these regions if successfully implemented. It would be instructive if these programmes could be used as a springboard for further collaboration regionally on the monitoring of POPs in the future.

The needs of the regions are varied in order to fully address the problems of environmental pollution from POPs. The present efforts being made by most countries to monitor POPs should be recognised and further development should be built on these ongoing initiatives. A major concern is the differing levels of priority placed on POPs control between countries. As the globe comes under increasing pressure from these migrating chemicals, more emphasis should be placed on developing regional collaboration given common environmental issues from POPs with these synergies feeding into a global programme that sets the conditions for all programmes to follow.

The transfer of technology must be undertaken in a systematic manner with developing countries agreeing to build capacity for monitoring that ensures efficiency and avoids overlap on the wider global scale. To do this, the strongest commitment possible should be sought to bind the countries under the Stockholm Convention so that fulfilment of targets can be achieved for all the chemicals selected throughout all matrices analysed.

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Global Network for Monitoring of Chemicals in The Environment and Emep

Prepared by the Chemical Co-ordinating Centre (CCC) and the Meteorological
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UNEP Chemicals, which is the centre for all chemicals-related activities of the United
Nations Environment Programme, has established the "Global Network for
monitoring of Chemicals in the Environment". The network will initially focus on the
twelve POPs subject of the Stockholm Convention on Persistent Organic Pollutants
and in the future enlarge its scope to other chemicals that will be considered as
priorities by the international community.

The Stockholm Convention on Persistent Organic Pollutants
The Stockholm Convention is a global treaty to protect human health and the
environment from persistent organic pollutants (POPs). The Convention includes two
articles that describe monitoring of POPs and evaluation of the monitoring. These two
articles are Article 11 ("Research, development and monitoring") and Article 16
("Effectiveness evaluation").

Article 11 "Research, development and monitoring" states that the Parties shall
encourage and/or undertake appropriate research, development, monitoring and
cooperation pertaining to persistent organic pollutants, including:
-   Sources and releases into the environment;
-   Presence, levels and trends in humans and the environment;
-   Environmental transport, fate and transformation;
-   Effects on human health and the environment;
-   Socio-economic and cultural impacts;
-   Release reduction and/or elimination; and
-   Harmonized methodologies for making inventories of generating sources and
    analytical techniques for the measurement of releases.

The Parties shall also support and further develop international programmes, networks
and organizations aimed at defining, conducting, assessing and financing research,
data collection and monitoring and support national and international efforts to
strengthen national scientific and technical research capabilities and to promote access
to, and the exchange of, data and analyses.

Article 16 "Effectiveness evaluation" states that the Conference of the Parties shall
evaluate the effectiveness of the Convention.

The Convention on Long Range Transboundary Air Pollution
The Convention on Long Range Transboundary Air Pollution (LRTAP), signed in 1979, has provided an effective framework to reduce air pollution in the UN/ECE region (http://www.unece.org/env/lrtap/). It has established a broad framework for cooperative action on reducing the impact of air pollution and sets up a process for negotiating concrete measures to control emissions of air pollutants through legally binding protocols. In this process, the EMEP programme (Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air pollutants in Europe) has been established with the main objective to regularly provide Governments and subsidiary bodies under the LRTAP Convention with qualified scientific information to support the development and further evaluation of the international protocols on emission reductions negotiated within the Convention.

Strategy for EMEP 2000-2009: Persistent organic pollutants
The main goals are:
- Quantification of national emissions, quantifying and minimizing emission uncertainty especially for pesticides
- Determination of the source-exposure relationships through improved understanding of exchange processes between atmosphere, soil, sea and biota.
- Improvement and validation of models leading to development of operational models
- Assessment of transboundary fluxes, as well as deposition and concentrations of selected POPs in the atmosphere, soil, sea and biota, to evaluate the harmful effects on ecosystems and human health
- Trend establishment for compliance
- Analysis of how different environmental compartments responds to emission reductions.

Cooperation with other programmes
Persistent organic pollutants (and heavy metals) were included in EMEP's monitoring program in 1999. However, already in 1995, co-operation concerning POPs between EMEP and other international programs was established. This co-operation included the establishment of a common database and collection of already available data on POPs among the participants. A number of countries have been reporting results within the EMEP area in connection with different national and international programmes such as HELCOM, AMAP, OSPARCOM and MEDPOP.

Comparison of the goals of "Global Network for monitoring of Chemicals in the Environment" and EMEP
The aims of monitoring as formulated in the Stockholm Convention and the EMEP strategy thus have much in common. In particular, both focus on the following topics:
- Quantifying national emissions
- Concentrations in the environment
- Trends
- Transport, transformations and fate
- Effects on the environment
- Harmonized methodologies

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In addition to the main topics mentioned above, EMEP focuses also on:
- Modelling to support the measurement data in order to fulfil the requirements of the CLRTAP
- Transboundary fluxes

The UNEP Chemicals Monitoring Network will focus on:
- Human health
- Socio-economic and cultural impacts
- Reduction of emissions

There are, however, also important differences. EMEP aims at linking emissions rates with deposition and exposure levels through the integration of observations with models describing the emissions, dispersion and deposition of pollutants and also their distribution in various media. UNEP currently does not aim at undertaking such modelling.

Measurement programme
The EMEP measurement programme includes inorganic compounds, heavy metals and particles, but also organic compounds such as light hydrocarbons, aldehydes, and POPs (PAH, PCB, HCB, chlordane, lindane, γ-HCH, DDT/DDE).

The intention of the Network is to initially establish a measurement programme that includes the twelve POPs specified in the Stockholm Convention.

Measurement sites
Initially, EMEP operated a measurement network in Europe. Lately, it has been extended to include contributions from North America in the west to Kazakhstan in the east. EMEP is thus no longer a regional activity in Europe, but is becoming part of a global network. EMEP has also established close cooperation with other regional and global monitoring programmes such as EANET and WMO-GAW, and EMEP also plays an important part in the EU/ESA activity GMES (Global Monitoring for Environment and Security).

The Global Network for monitoring of Chemicals in the Environment aims at establishing a global monitoring and will therefore not be limited to Europe.

Main components of the EMEP system
A coherent strategy

EMEP has elaborated over the past years a cost-effective monitoring strategy to fulfil its objectives, which are in large parts overlapping with those of UNEP.

A network of measurement sites
The measurement network of EMEP focuses on Europe, but the system can easily be adjusted to meet the needs of a global monitoring network.

Adopted protocols for sampling and analysis
In order to assure comparability of the generated data, it is necessary to harmonise the methods used for sampling and analysis. In EMEP, these methods are described in

detailed manuals that are discussed and adopted by national experts in collaboration with the EMEP centres.

Quality control/quality assurance

Even though protocols for sampling and analysis have been adopted (see above), it is important to monitor data quality of the network on a routine basis. In EMEP, this is mainly done by interlaboratory comparisons that are carried out on a regular basis.

A fully working system for data handling, data storing and data dissemination

An essential part of the EMEP programme is that the generated data are collected and stored in a common database, in an agreed format, together with necessary additional information. The database also contains information on data quality. The database also enables extensive data dissemination within the whole network and facilitates use by external experts.

Modelling/measurement approach

In view of the expensiveness of POP measurements, it is important to complement measurements by modelling, so that available resources are used as effectively as possible. Apart from direct evaluation of pollution levels, pathways of transport and trends and projections in the environment, modelling output can be useful for further development of the measurement network. E.g., models can be used to derive optimised recommendations for measurements (period, frequency, site locations). Some POPs have the potential for long-range transport at a global scale. It is therefore necessary to conduct POP modelling with hemispheric or global models. EMEP has accordingly extended its modelling domain for POPs to the hemispheric scale.

The results of measurement/modelling evaluation of contamination levels for selected POPs are already included in a number of studies performed within the framework of various international organizations and conventions (UNEP, AMAP, WMO, WHO, HELCOM). Some examples are the UNEP/GEF Project "Regionally Based Assessment of Persistent Toxic Substances" (RBA PTS), the WHO project "Health Risks of Persistent Organic Pollutants from Long-Range Transboundary Air Pollution", a number of reports on evaluation of pollution of the Baltic Sea under HELCOM and others.

Conclusions

Monitoring is expensive and it is important that the available resources are used as effectively as possible.

By adopting the EMEP-system, with necessary adjustments, the Global Network for monitoring of Chemicals in the Environment will achieve the following:
- Cost-effective establishing of the network
- A well-established and tested operating system
- Comparability between two important international monitoring networks

7. DECISION INC-6/17: EFFECTIVENESS EVALUATION

The Intergovernmental Negotiating Committee

Requests the secretariat to begin to address the environmental monitoring and evaluation needs as described in article 16 of the Stockholm Convention on Persistent Organic Pollutants for chemicals included in annexes A, B, and C of the Convention and in doing so to:

(a) Develop guidance on the nature of the effectiveness evaluation;

(b) Identify the basic data needed to support the effectiveness evaluation;

(c) Assess the capacity of existing monitoring programmes to make available necessary monitoring data and then begin making arrangements for the provision of comparable monitoring data for the effectiveness evaluation. This can be assisted by continuing the work initiated by UNEP Chemicals for the substances listed in annexes A, B, and C;

(d) Identify where suitable monitoring data are not available;

(e) Compile guidance for the collection of data and, subject to the availability of additional external funding, test the guidance by developing a pilot project in one or more regions;

(f) Facilitate arrangements to obtain appropriate monitoring information on annexes A, B, and C substances for regions where such information would not otherwise be available, taking into consideration that cost effectiveness in other regional evaluations has been achieved by using a tiered approach (e.g. one which centralizes the most advanced laboratory capacity at regional nodes);

(g) Report on progress to the Intergovernmental Negotiating Committee at its
(h) seventh session.

UNEP Workshop to Develop a Global POPs Monitoring Programme to Support the Effectiveness Evaluation of the Stockholm Convention

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