UNITED NATIONS

UNEP

SC

UNEP/POPS/COP.10/INF/42

Distr.: General
21 April 2021

English only

Stockholm Convention on Persistent Organic Pollutants

Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants
Tenth meeting
Geneva (online), 26–30 July 2021*
Item 5 (i) of the provisional agenda**

Matters related to the implementation of the Convention: effectiveness evaluation

Guidance on the global monitoring plan for persistent organic pollutants

Note by the Secretariat

As is mentioned in the note by the Secretariat on the global monitoring plan for effectiveness evaluation (UNEP/POPS/COP.10/18), the updated guidance on the global monitoring plan for persistent organic pollutants prepared by the global coordination group is set out in the annex to the present note. The present note, including its annex, has not been formally edited.

* Face-to-face resumed meetings of the conferences of the Parties to the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal, the Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade and the Stockholm Convention on Persistent Organic Pollutants are tentatively scheduled to take place in 2022.

** UNEP/POPS/COP.10/1.

Annex

GUIDANCE ON THE GLOBAL MONITORING PLAN FOR PERSISTENT ORGANIC POLLUTANTS

January 2021

ACKNOWLEDGEMENT

This guidance document has been reviewed and updated by the members of the global coordination group for the global monitoring plan: Mr. Martin Benoit Ngassoum (Cameroon), Mr. Vincent Odongo Madadi (Kenya), Mr. Otmani Anas (Morocco), Mr. Minghui Zheng (China), Mr. Johann Poinapen (Fiji), Mr. Yasuyuki Shibata (Japan), Ms. Kateřina Šebková (Czech Republic), Mr. Trajce Stafilov (Republic of North Macedonia), Ms. Zarema Amirova (Russian Federation), Ms. Sandra De Souza Hacon (Brazil), Ms. Alejandra Torre (Uruguay), Mr. Rigoberto Blanco (Costa Rica), Ms. Sara Broomhall (Australia), Mr. Tom Harner (Canada), and Mr. Ramon Guardans (Spain).

The following experts are also gratefully acknowledged for their valuable contributions to the previous updates of this guidance document: Ms. Maria Tominaga, Mr Gilberto Fillman (Brazil), Mr. Derek Muir, Mr. Tom Harner* (Canada), Mr. Minghui Zheng* (China), Ms. Jana Klanova, Ms. Katerina Sebkova* (Czech Republic), Ms. Karin Malisch, Mr. Rainer Malisch (Germany), Mr. Yasuyuki Shibata* (Japan), Mr. Vincent Madadi (Kenya)*, Mr. Mohamed Kabriti (Morocco), Mr. Ramon Guardans* (Spain), Ms. Heidelore Fiedler, Ms. Linda Liderholm* (Sweden), Ms. Alejandra Torre* (Uruguay). In addition, the members of the regional organization groups for the global monitoring plan have also been consulted in the process for review and update: Mr. Martin Benoit Ngassoum (Cameroon), Mr. Jean de Dieu Nzila (Rep. of Congo), Mr. Vincent Odongo Madadi (Kenya), Mr. Taelo Letsela (Lesotho), Ms. Halimatou Kone Esp Traore (Mali), Mr. Otmani Anas (Morocco), Mr. Minghui Zheng (China), Mr. Johann Poinapen (Fiji), Mr. Dinesh Runiwal (India), Mr. Abdulrahman Bahrami (Iran), Mr. Yasuyuki Shibata (Japan), Mr. Anas Ali Saeed Al-Nadhari (Yemen), Ms. Anahit Aleksandryan (Armenia), Ms. Kateřina Šebková (Czech Republic), Mr. Trajce Stafilov (Macedonia FYR), Ms. Anna Cumanova (Moldova), Ms. Zarema Amirova (Russian Federation), Ms. Sandra De Souza Hacon (Brazil), Mr. Rigoberto Blanco (Costa Rica), Ms. Carola Resabala Zambrano (Ecuador), Ms. Trecia David (Guyana), Mr. Arturo Gavilan (Mexico), Ms. Alejandra Torre (Uruguay), Ms Sara Broomhall (Australia), Mr. Tom Harner (Canada), Mr. Peter Korytar (European Commission), Ms. Katrine Borga (Norway), Mr. Ramon Guardans (Spain), and Ms. Linda Linderholm (Sweden).

The following experts have provided initial contributions to the production of the preliminary version of the guidance document: Mr. Juan Carlos Colombo (Argentina); Mr. Lars-Otto Reiersen (AMAP); Mr. Tom Harner (Canada); Mr. Oladele Osibanjo (Nigeria); Mr. Janneche Utne Skaare (Norway); Mr. Hindrik Bouwman, (South Africa); Mr. Anders Bignert (Sweden); Mr. Bo Jansson (Sweden); Mr. Bo Wahlström (Sweden); Ms. Heidelore Fiedler (UNEP/DTIE Chemicals Brach); Mr. Jørgen Schlundt (WHO).

Initial input was also provided by further members of the Provisional Technical Working Group for the global monitoring plan: Mr. Peter Weiss (Austria), Ms. Therese Yarde (Barbados), Mr. Mansourou Moudachirou (Benin), Ms. Tsvetanka Dimcheva (Bulgaria), Mr. Indrani Chandrasekharan (India), Mr. Demba Sidibe (Mali), Mr. Nee Sun Choong Kwet Yive (Mauritius), Ms. Anna Cumanova (Moldova) and Mr. Tor Johannessen (Norway).

The support from Stockholm Convention Secretariat technical staff and contribution from UNEP/DTIE Chemicals Brach for the production of the initial draft is gratefully acknowledged. These contributions include input from Mr. David Stone, Mr. Frank Wania, Ms. Pierrette Blanchard, Mr. Len Barrie and Mr. José Sericano.

* Also members of the regional organization groups and/or the global coordination group for the global monitoring plan.

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LIST OF ABBREVIATIONS AND GLOSSARY OF TERMS

List of abbreviations

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

IP/RP	International/regional programmes
IPCS	International Programme on Chemical Safety
JECFA	Joint FAO/WHO Expert Committee on Food Additives
LOD	Limit of detection
LOQ	Limit of quantification
LRM	Laboratory reference material
LRMS	Low resolution mass spectrometer
LRTAP	Long Range Transboundary Air Pollution Convention (under the auspices of UNECE)
LRTP	Long-range transport potential
MDL	Method detection limit
mL	Milliliter
MONARPOP	Monitoring Network in the Alpine Region for Persistent Organic pollutants
MS	Mass selective detector
NGOs	Non-governmental organisations
OC	Organochlorine
OCP	Organochlorine pesticide
OECD	Organisation for Economic Co-operation and Development
OSPAR	Oslo Paris Commissions, Convention for the Protection of the Marine Environment of the North East Atlantic
PBDE	Polybrominated diphenyl ether
PCA	Pentachloroanisole
PCB	Polychlorinated biphenyls
PCDD	Polychlorinated dibenzo-*para*-dioxins
PCDF	Polychlorinated dibenzofurans
PCN	Polychlorinated naphthalenes
POPs	Persistent organic pollutants
PRTRs	Pollutant release and transfer registers
PTS	Persistent toxic substances
PUF	Polyurethane foam
QA/QC	Quality assurance and quality control regimes
ROGs	Regional organization groups for the Global Monitoring Plan
SCCPs	Short-chain chlorinated paraffins
SMOC	The Sound Management of Chemicals (SMOC) initiative under the North American Agreement on Environmental Cooperation (NAAEC)
SOP	Standard operating procedure
TCDD	Tetrachlorodibenzo-*para*-dioxin
TEF	Toxic equivalency factor
TEQ	Toxicity equivalents
UNECE	United Nations Economic Commission for Europe
UNEP	United Nations Environment Programme

WHO	World Heath Organization
WMO	World Meteorological Organization
XAD	Styrene/divinylbenzene-co-polymer resin

Glossary of terms

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

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

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1 BACKGROUND AND OBJECTIVES

The Stockholm Convention on Persistent Organic Pollutants (POPs) was adopted on 22 May 2001 and entered into force on 17 May 2004. As of January 2021 the Convention had 184 Parties.

The objective of the Stockholm Convention on POPs is to:

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

Article 16 of the Stockholm Convention requires the Conference of the Parties to evaluate periodically whether the Convention is effective in achieving this objective. This evaluation is to be based on:

- Comparable and consistent monitoring data on the presence of POPs in the environment and in humans pursuant to paragraph 2 of Article 16;
- Information provided through the national reports submitted pursuant to Article 15;
- Non-compliance information under Article 17.

The Global Monitoring Plan is implemented by the regional organization groups established in the five United Nations regions (decision SC-3/19). The main objective of the regional organization groups is to define and implement the strategy for regional information gathering, including facilitating capacity enhancement, and to produce the regional monitoring reports. A global coordination group, comprising of three members from each regional organization group, is in place to harmonize and coordinate implementartion activities among the UN regions, to produce the global monitoring report, and to maintain up-to-date the guidance on the Global Monitoring Plan. The terms of reference of the regional organization groups and the global coordination group are included in the annex to decision SC-8/19.

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

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

The guidance document should be viewed as one part of an evolving set of documents that inform the reader about environmental information gathering and reporting methodologies to support effectiveness evaluation. In terms of increasing complexity, these documents include the following: Article 16 of the Convention; relevant decisions of the Conference of the Parties; the Global Monitoring Plan and its implementation plan; and the guidance document. The most recent versions of these documents are available at http://chm.pops.int.

The guidance document is continuously updated by the global coordination group for the global monitoring plan to include the most recent technical and scientific information and to address monitoring needs for new chemicals (sampling and analysis), as they are listed in the annexes to the Convention, with the assistance of invited experts, as necessary. The most recent version of the guidance should always be used as the reference document.

1.1 The objectives of the POPs Global Monitoring Plan

To evaluate whether releasesof POPs are reduced or eliminated as requested by Articles 3 and 5 of the Convention, information on environmental levels of the chemicals listed in the Convention should enable detection of trends over time. Therefore, focus is upon monitoring of background levels of POPs at locations not influenced by local sources. Reliable identification of trends will require that statistical

evaluation is carried out on the design of each national monitoring programme contributing to the Global Monitoring Plan, to ensure that it is powerful enough to detect trends in time.

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

> Provide a harmonized organizational framework for the collection of comparable monitoring data on the presence of the POPs listed in Annexes A, B and C of the Convention in order to identify trends in levels over time as well as to provide information on their regional and global environmental transport.

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

1.2 The objectives of the guidance document

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

The objective of the guidance document is therefore to:

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

This framework aims to assist programmes initiated specifically for the purposes of Article 16 and existing programmes that may wish to contribute to the Article 16 monitoring reports. It also helps laboratories identified through the inventory building process in developing their capacity and in preparing targeted proposals for support from their government or from other donors.

The first edition (2007) of the guidance document was focused on the requirements to prepare for the first effectiveness evaluation. The second edition (2015) addressed the listing of new POPs under the Convention by proposing adequate sampling methodologies for all compounds listed in the Convention until 2013. This third edition (2019) addresses new POPs listed in 2015 and 2017 as well as lessons learned during implementation of the second GMP phase (2009-2015). The guidance is intended to be a living framework, that may evolve and be elaborated over time to reflect further direction from the Conference of the Parties, experience gained and emerging specific needs.

1.3 General principles

The framework for the Global Monitoring Plan closely follows the direction given by the Conference of the Parties.

The Global Monitoring Plan should:

- Outline a strategic and cost-effective approach and build on, but not be limited to, existing and scientifically sound human health and environmental monitoring programmes to the extent possible, with the aim of providing appropriate and sufficient comparable data for the effectiveness evaluation of the Convention;
- Ensure and enhance comparability and consistency in monitoring data;
- Be practical, feasible and sustainable;
- Be inclusive, achieve global coverage and contain at least core representative data from all regions;
- Be designed to go beyond the first monitoring report and address long-term needs for attaining appropriate representative data in all regions;

- Provide for supplementing data, where necessary, taking into account the differences between regions and their capabilities to implement monitoring activities;
- Enable phased enhancement of the ability of Parties to participate in regional arrangements for producing comparable data.

According to the conclusions and recommendations of the report on effectiveness evaluation:

> The Global Monitoring Plan provides the necessary environmental monitoring information to fully support the evaluation of the effectiveness of the Convention, and therefore should be sustained in the long term to enable it to continue to provide valuable data for effectiveness evaluation.

Substantial geographic differences existed in the availability of monitoring capacity to contribute comparable data and information for the purpose of the effectiveness evaluation of the Stockholm Convention. Systematic capacity building activities have been carried out in developing countries, including strategic partnerships with well-established monitoring programmes. Despite these efforts, several regions still have limited capacity to monitor POPs. The addition of new POPs to the Convention creates additional demand to implement and sustain POPs monitoring activities. A number of tasks to identify needs and opportunities to increase participation and ensure sustanbility of activities have been identified as follows:

- A comprehensive regional inventory of capacities should be developed and maintained;
- Regions maintaining or seeking to build and/or enhance capacity should be encouraged and supported to form and /or maintain strategic partnerships with existing monitoring programmes;
- Continued support to existing and new monitoring activities is required to ensure continuity in sampling, analysis, and data QA/QC and storage, in order to provide adequate data to assess temporal trends and long-range transport of POPs;
- Laboratories in programmes contributing monitoring data to the GMP should participate in international interlaboratory assessments;
- Efforts to address remaining gaps in data coverage and to monitor new POPs as they are added to the Convention should be intensified and diversified;
- Regional communication, coordination and information exchange structures to enhance information sharing among the regional organization groups should be strengthened;
- Regional organization groups and regional centers should strive to improve intra-regional coordination among experts (including academia) to address GMP data requirements;
- The regional and global monitoring reports should be broadly shared;
- The GMP data warehouse should be serviced and supported to support data handling in the frame of the GMP and to provide access to up-to-date POPs monitoring data.

Additional funding and resources will be needed to respond to pressures for analysis of new POPs. In addition, monitoring programmes may need to adjust their protocols and resources to better align with new priorities. Some pressure can be relieved by reducing analysis frequency for legacy POPs (e.g. PCB, organochlorine pesticides) where declining trends have been established, optimizing analytical methods, and establishing partnerships among laboratories to address specialized analytical needs. It is not necessary for every laboratory to be an expert for every class of POPs.

1.4 Sustainability and Adaptability of the GMP

A rigorous and continuous long-term monitoring programme for POPs in core media (air, human tissues, and water for PFASs) is an absolute necessity to fulfill the scientific basis and requirements of Article 16. With three phases of implementation of the GMP since the entry into force of the Convention as of September 2020, several long-term programs have reported consistently on the temporal trends on POPs and in some cases have extended their scope to address regional data gaps that have been identified. New programs have also been implemented to address data gaps and are establishing new baselines for future trends assessment.

The Stockholm Convention is a dynamic treaty. Since its entry into force in 2004 the number of POPs has increased from the original 12 to, as of 2020, 30 chemicals and/or groups of chemicals The process for evaluation and listing of further chemicals in the Convention will continue in the future. Consequently,

monitoring programmes for POPs will need to adapt to the additional requirements for POPs monitoring. At the same time, monitoring programmes are also adjusting to advances in science by incorporating new methodologies in sampling and analysis, including new understanding in the interpretation of monitoring data. These measures are needed to ensure that their programs are current, adaptable, relevant and ultimately sustainable for the long-term.

Several topics have been highlighted as key requirements for the continual advancement of the GMP (UNEP 2009, 2017, 2019). These are summarized below according to goals, challenges, and opportunities and strategies associated with a sustainable and forward-looking GMP.

GMP Goals:

- long-term and reliable measurements of POPs in core media with good coverage in all 5 UN regions.
- systems and tools for storing and sharing data (e.g. GMP Database) and expertise (e.g. ROGs and experts) for interpreting and reporting results according to the GMP reporting cycle.
- cooperation within and between regions in terms of information sharing, technology transfer, capacity building, and training.

GMP Challenges:

- growing list of POPs is contributing to analysis and reporting requirements for monitoring programs
- highly specialized analytical equipment and methods are required for some POPs, especially for detection at trace levels e.g. in air.
- rising costs associated with additional POPs and analytical needs is increasing pressure on long-term programs and diminishing feasibility of establishing new programs.
- interpreting trends for a growing list of POPs and incorporating new thinking related to chemical mixture (which include transformation products and non-targeted analysis) (Ref – Science) rather on a chemical-by-chemical basis. Trying to relate this to the fundamental goal of the Convention to “protect human health and the environment from the harmful effects of POPs”.

GMP Opportunities and Strategies:

- forming intra- and inter-regional partnerships and expertise/resource-sharing to help address challenges with a dynamic and growing GMP.
- using emissions and other relevant information (e.g. satellite data), models, and other expertise to interpret existing data and to advise and prioritize on the data needs of the GMP in terms of reporting and required frequency of analysis/sampling for different POPs.
- improving data accessibility and integrity by making use of the GMP database and other databases for archiving data, making them openly accessible, and linking to Global Earth Observations to allow for the multidimensional analyses.
- sample archiving (or “banking” – see Chapter 8) for future retrospective analysis of POPs
- making use of monitoring data from existing long-term programs for “other media” (i.e. non-core media) to gain insight on regional trends of POPs, especially in regions where trend information in core media is lacking or just starting. In addition, the “other media” information could be used for optimization of core media activities.
- using new science/tools (e.g. non-target analysis, toxicogenomics) to consider the cumulative impact of different POPs classes (including transformation products) as mixtures of chemicals to which humans and the environment are exposed and related implications for effectiveness evaluation.
- better communication and coordination among international groups and programs that are tackling the POPs problem from different but related angles, to ensure that the best decisions are being made. These groups include, inter alia, GMP (GMP (ROG members and experts), the

POPRC, modelers (e.g. UNECE LRTAP/ task force on HTAP), AMAP, WHO and external bodies and activities (GEF, SAICM, GEO) and activities (EU Framework Programmes on Research and Development - Horizon 2020).

Existing POPs monitoring activities in core matrices (air and human breast milk) have been used for over a decade and have successfully provided data for preparation of the regional and global monitoring reports.

Recommendations of the GMP global coordination group and regional oganizuation groups to guide further POPs monitoring activities in line with the current three principles/paradigms are as follows:

- Long term availability and comparability of data in core media is crucial for successful continuity of the Global monitoring plan in the future;
- A successful monitoring, sampling and analysis of POPs can be sustainable and high quality maintained if the activities are linked to a solid infrastructure and reliable monitoring operations/systems;
- Dynamic nature of the Stockholm Convention and its widening scope requires pragmatic actions to relieve pressures on global analytical abilities and capacities.

Essential and most feasible requirements for a global, sustainable and technically sound POPs monitoring programme include:

Air

Strategic partnerships with international monitoring programs on ambient air POPs monitoring has been developed since early 2000. Activities are harmonized and intercalibrated and cost effective. The programs provide archive opportunities. The arrangements need to be continued, strengthened/optimized with priority to support long-term trends and bridge gaps found in existing networks. The existing international/global POPs monitoring networks are open to inclusion of additional sampling sites measuring the background concentrations that complement the missing knowledge and provide for long term trends and long range transport data to support interpretation.

Human milk

The current arrangements and support provided by UNEP for monitoring POPs in human milk is very efficient and cost-effective. It has provided a valuable archive of samples and results for future analysis, as needed. The human milk POPs monitoring program (survey) must be continued by using the same model (centrally organized by UNEP once per five years, same sampling protocol, one laboratory analyzing results, focus on trends) in order to correctly assess trends of POPs in humans.

Water

The water POPs monitoring program must be further developed and consolidated in terms of medium, sampling sites, and substances measured. Focus of activities is identification of trend data, however it is necessary to align existing international activities and explore the potential to regional trend interpretation.

Crosscutting elements:

- Continuous updates of monitoring tools and GMP guidance document adapting it to widening scope of the Convention and advances in research;
- Partnering with modellers to improve interpretation and understanding regarding:
    - factors influencing temporal trend data (e.g. climate change) and the required frequency of data/reporting for different POPs in the future;
    - the role of primary versus secondary emissions and how these relate to observed temporal trends in core media, and mitigation success in the context of Effectiveness Evaluation (Article 16).
- Linking to other available sources of data such as satellites to improve interpretation;
- Interlaboratory Assessment programme for dataproviders to organize an effective and cost efficient QA/QC.

2 SUBSTANCES TO BE MONITORED

2.1 Background

The objective of the Stockholm Convention is to protect human health and the environment from POPs with the ultimate goal to eliminate them, where feasible. An obvious way to evaluate the effectiveness of the Convention is to measure the concentration of the POPs listed in Annexes A, B, or C of the Convention in relevant matrices (see Chapter 4). As of January 2019, the Convention lists 30 POPs, which include the following substances or groups of substances (in alphabetical order; the meetings of the Conference of the Parties at which the listing of the chemicals took place are inidcated in parenthesis):

1. Aldrin
2. Alpha-hexachlorocyclohexane (α-HCH) (COP-4, 2009)
3. Beta-hexachlorocyclohexane (β-HCH) (COP-4, 2009)
4. Chlordane
5. Chlordecone (COP-4, 2009)
6. Decabromodiphneyl ether (COP-8, 2017)
7. Dichlorodiphenyltrichloroethane (DDT)
8. Dicofol (COP-9, 2019)
9. Dieldrin
10. Endosulfan (COP-5, 2011)
11. Endrin
12. Gamma-hexachlorocyclohexane (γ-HCH) (COP-4, 2009)
13. Heptachlor
14. Hexabromobiphenyl (HBB) (COP-4, 2009)
15. Hexabromocyclododecane (HBCD) (COP-6, 2013)
16. Hexabromodiphenyl ether and heptabromodiphenyl ether (PBDE) (COP-4, 2009)
17. Hexachlorobenzene (HCB)
18. Hexachlorobutadiene (COP-7, 2015 and COP-8, 2017)
19. Mirex
20. Pentachlorobenzene (PeCBz) (COP-4, 2009)
21. Pentachlorophenol, its salts and esters (COP-7, 2015)
22. Perfluorooctane sulfonic acid (PFOS) (COP-4, 2009)
23. Perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds (COP-9, 2019)
24. Polychlorinated biphenyls (PCB)
25. Polychlorinated dibenzo-*para*-dioxins (PCDD)
26. Polychlorinated dibenzofurans (PCDF)
27. Polychlorinated naphthalenes (PCN) (COP-7, 2015)
28. Short-chain chlorinated paraffins (SCCPs) (COP-8, 2017)
29. Tetrabromodiphenyl ether and pentabromodiphenyl ether (PBDE) (COP-4, 2009)
30. Toxaphene

The above list reflects the status as of January 2019; further chemicals may be listed to either of the three Annexes to the Convention by the Confernce of the Parties. To date, two more chemicals have been recommended for listing by the POPs Review Committee and one is under evaluation. Newly listed POPs would be further included in the global monitoring plan and this chapter would be modified accordingly.

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

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

POP	Acronym	Parent compound[1]
Initial 12 POPs		
Aldrin		Single compound
Chlordane		2 isomers
Dichlorodiphenyltrichloroethane	DDT	2 isomers
Dieldrin		Single compound
Endrin		Single compound
Hexachlorobenzene	HCB	Single compound
Heptachlor		Single compound
Mirex		Single compound
Polychlorinated biphenyls	PCB	209 congeners
Polychlorinated dibenzo-*p*-dioxins	PCDD	75 congeners
Polychlorinated dibenzofurans	PCDF	135 congeners
Toxaphene		Technical mixtures of chlorinated bornanes and chlorinated camphenes (about 16,000 congeners or isomers)
POPs listed at COP-4		
Chlordecone (UNEP, 2009c)		Single compound
alpha-Hexachlorocyclohexane (UNEP, 2009a)	α-HCH	Single compound; isomer to β-HCH and γ-HCH
beta-Hexachlorocyclohexane (UNEP, 2009b)	β-HCH	Single compound; isomer to α-HCH and γ-HCH
Lindane, gamma-Hexachlorocyclohexane (UNEP, 2009f)	γ-HCH	Single compound; isomer to α-HCH and β-HCH
Hexabromobiphenyl (UNEP, 2009d)	HBB	42 isomers in one homolog group
Pentachlorobenzene (UNEP, 2009g)	PeCBz	Single compound
Tetrabromodiphenyl ether and penta-bromodiphenyl ether (commercial pentabromodiphenyl ether) (UNEP, 2009i)	c-penta BDE	Two homolog groups: 42 tetrabrominated isomers 46 pentabrominated isomers
Hexabromodiphenyl ether and heptabromodiphenyl ether (commercial octabromodiphenyl ether) (UNEP, 2009e)	c-octa BDE	Two homolog groups: 42 hexabrominated isomers 24 heptabrominated isomers

[1] Theoretical number of congeners or structural isomers within this chemicals' group.

Perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride (UNEP, 2009h)	PFOS	Single anionic compound with one linear (L-PFOS) and many branched isomers
POPs listed at COP-5		
Endosulfan; technical and its related isomers (UNEP, 2011)		Single compound; mixture of stereoisomers
POPs listed at COP-6		
Hexabromocyclododecane (UNEP, 2013)	HBCD	3 structural isomers
POPs listed at COP-7		
Polychlorinated naphthalenes (*di-*, *tri-*, *tetra-*, *penta-*, *hexa-*, *hepta-*, and *octa*chlorinated naphthalenes) (UNEP, 2015c)	PCN	73 congeners (*di-* to *octa*chlorinated)
Hexachlorobutadiene (UNEP, 2015a, 2017a)	HCBD	Single compound
Pentachlorophenol and its salts and esters (UNEP, 2015b)	PCP	Single anionic compound
POPs listed at COP-8		
Short-chain chlorinated paraffins (with chain lengths ranging from C_{10} to C_{13} and a content of chlorine greater than 48 per cent by weight) (UNEP, 2017b)	SCCP	Four homolog groups with skeleton of linear C_{10}, C_{11}, C_{12} or C_{13}; and varying degrees of chlorination; several thousand congeners (theoretically)
Decabromodipheyl ether	Deca-BDE	Single compound
Hexachlorobutadiene (UNEP, 2015a, 2017a)	HCBD	Single compound
POPs listed at COP-9		
Dicofol		2 isomers
Perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds		Single linear anionic compound with branched isomers

The following substances are under review by the POPs Review Committee (status 2021):

Candidate POPs under review (status 2021)		
	Acronym	**Parent compound[2]**
UV-328		Single compound
Dechlorane Plus		2 isomers
Methoxychlor		Single compound
Perfluorohexane sulfonic acid	PFHxS	Single linear anionic compound with branched isomers

2.2 Recommendations for POPs to be analyzed

Based on recommendations from three workshops of the GMP Expert Group that considered the 2nd revision of the Guidance document for the GMP, held in April and September 2010 in Geneva (UNEP 2010), an expert workshop on perfluorinated compounds, held in October 2014 in Amsterdam, the Netherlands (UNEP 2014), and the meeting of the GMP expert group, held in Brno, Czech Republic in

[2] Theoretical number of congeners or structural isomers within this chemicals' group.

2017 (UNEP 2018) as well as experiences from GMP implementation projects, details have been added as to the chemical identification of the POPs. It shall be noted that the listing of the POPs does not necessarily specify the analytes – although CAS numbers are provided in the listing – and because it may not be necessary or even possible to analyze all individual congeners of the mixtures in the above list, the following chemical substances are recommended for analysis (see Table 2.2). Substances in Table 2.2 include the parent POPs but also some major transformation products that are covered under the Convention. In the case of PFOS (UNEP, 2009h), decision SC-4/17 includes precursor compounds that are especially relevant for understanding long-range transport in air.

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

Water is recommended as a core matrix for fluorinated POPs only; thus, chlorinated and brominated POPs shall not be analysed in water.

For POPs presented in square brackets, the recommended analytes are either not yet defined, *e.g.,* for PCN or SCCPs, or the presence of these POPs (or their transformation products) in environmental or human matrices under normal conditions are not yet confirmed (dicofol, PCP). Present projects by various research groups assist with decision making and recommendations.

The environmental and human monitoring under the GMP is to be undertaken regionally while also achieving global coverage. Highest requirements on analytical performance are therefore needed to identify small changes in concentrations.

For the Global Monitoring Plan (GMP), it is recommended to collect data for all 30 POPs (parent compounds, precursor and transformation compounds as shown in Table 2.2 below) in the recommended matrices (see Chapter 4).

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

	Compounds to be Monitored			
	Air	**Human Milk**	**Human Blood**	**Water**
Initial POPs				
Aldrin	Aldrin	Aldrin	Aldrin	Water has not been recommended as a core matrix for the lipophilic and nonpolar initial twelve POPs; therefore, analysis of surface waters is not recommended
Chlordane	*cis*- and *trans*-chlordane; and *cis*- and *trans*-nonachlor, oxychlordane	*cis*- and *trans*-chlordane; and *cis*- and *trans*-nonachlor, oxychlordane	*cis*- and *trans*-chlordane; and *cis*- and *trans*-nonachlor, oxychlordane	
DDT	4,4'-DDT, 2,4'-DDT and 4,4'-DDE, 2,4'-DDE, 4,4'-DDD, 2,4'-DDD	4,4'-DDT, 2,4'-DDT and 4,4'-DDE, 2,4'-DDE, 4,4'-DDD, 2,4'-DDD	4,4'-DDT, 2,4'-DDT and 4,4'-DDE, 2,4'-DDE, 4,4'-DDD, 2,4'-DDD	
Dieldrin	Dieldrin	Dieldrin	Dieldrin	
Endrin	Endrin	Endrin	Endrin	
HCB	HCB	HCB	HCB	
Heptachlor	Heptachlor and heptachlorepoxide	Heptachlor and heptachlorepoxide	Heptachlor and heptachlorepoxide	
Mirex	Mirex	Mirex	Mirex	
PCB	ΣPCB_6 (6 congeners): 28, 52, 101, 138, 153, and 180	ΣPCB_6 (6 congeners): 28, 52, 101, 138, 153, and 180	ΣPCB_6 (6 congeners): 28, 52, 101, 138, 153, and 180	
	PCB with TEFs* (12 congeners): 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189	PCB with TEFs* (12 congeners): 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189	PCB with TEFs* (12 congeners): 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189	
PCDD/PCDF	2,3,7,8-substituted PCD/PCDF (17 congeners)	2,3,7,8-substituted PCD/PCDF (17 congeners)	2,3,7,8-substituted PCD/PCDF (17 congeners)	
Toxaphene	Congeners P26, P50, P62	Congeners P26, P50, P62	Congeners P26, P50, P62	

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

POPs listed at COP-4				
	Air	Human Milk	Human Blood	Water
Chlordecone	Chlordecone	Chlordecone	Chlordecone	-
α-HCH	α-HCH	α-HCH	α-HCH	
β-HCH	β-HCH	β-HCH	β-HCH	
γ-HCH	γ-HCH	γ-HCH	γ-HCH	
Hexabromobiphenyl	PBB 153	PBB 153	PBB 153	
Pentachlorobenzene	PeCBz	PeCBz	PeCBz	
c-penta BDE c-octa BDE	PBDE 47, 99, 153, 154, 175/183 (co-eluting) Optional: PBDE 17, 28, 100	PBDE 47, 99, 153, 154, 175/183 (co-eluting) Optional: PBDE 100	PBDE 47, 99, 153, 154, 175/183 (co-eluting) Optional: PBDE 100	
PFOS[3]	PFOS, NMeFOSA, NEtFOSA, NMeFOSE, NEtFOSE (linear and branched)	PFOS (linear and branched)	PFOS (linear and branched)	PFOS (linear and branched)
POPs listed at COP-5				
Endosulfan	α-, β-endosulfan; and endosulfan sulfate	α-, β-endosulfan; and endosulfan sulfate	α-, β-endosulfan; and endosulfan sulfate	-
POPs listed at COP-6				
HBCD	α-HBCD, β-HBCD, γ-HBCD	α-HBCD, β-HBCD, γ-HBCD	α-HBCD, β-HBCD, γ-HBCD	-
POPs listed at COP-7				
PCN	CN27/30, CN52/60, CN66/67 and CN73	CN27/30, CN52/60, CN66/67 and CN73	CN27/30, CN52/60, CN66/67 and CN73	-
HCBD	HCBD	HCBD	HCBD	
PCP and its salts and esters	PCP, PCA	PCA	PCA	

[3] Referring to PFOS anion with linear and branched isomers.

POPs listed at COP-8				
SCCP (C_{10}-C_{13}) alkanes	SCCPs*	SCCPs*	SCCPs*	-
Deca-BDE	PBDE-209	PBDE-209	PBDE-209	
POPs listed at COP-9				
Dicofol	Dicofol	Dicofol	Dicofol	-
PFOA	PFOA	PFOA	PFOA	PFOA

* Sum SCCP based on congener-group specific quantification (see Chapter 5)

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

Candidate POPs under review (status 2021)				
	Air	**Human Milk**	**Human Blood**	**Water**
UV-328	UV-328	UV-328	UV-328	
Dechlorane Plus	Dechlorane Plus	Dechlorane Plus	Dechlorane Plus	-
Methoxychlor	Methoxychlor	Methoxychlor	Methoxychlor	-
PFHxS	PFHxS	PFHxS	PFHxS	PFHxS

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

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

2.3 Recommended reporting format

Spreadsheets to report the analytical data are available in EXCEL® format at http://www.pops-gmp.org. These spreadsheets contain the individual analytes as shown in Table 2.2 and the sum parameters for groups or mixtures of POPs. Some recommendations on how to report the concentrations include the following:

For **PCB**, it is recommended to analyze and report the six congeners individually to allow calculation of the sums of these six PCB (ΣPCB(6)).

For **PFOS**, it is recommended to report the concentrations of the linear PFOS (L-PFOS) anion and the sum of the branched PFOS (br-PFOS) anions and then, sum-up to the total PFOS $\Sigma PFOS_{total}$) (UNEP 2014).

For the **polybrominated diphenyl ethers (PBDE)**, three individual listings have occurred. The respective congeners in each of the listings – c-penta, c-octa, deca - shall be analysed and summed-up together with the sum of these congeners (ΣPBDE(6) or ΣPBDE(7) with PBDE-100 and ΣPBDE(9) for air including degradation products).

Although the hexachorocyclohexanes - α-HCH, β-HCH, lindane - have been listed separately, it is recommended to report the sum of these three as well ΣHXH(3)).

For endosulfans, the α- and β-isomers as well as the sulfonate shall be reported together with the sum of these three (Σendosulfans(3)).

For HBCD, the concentrations of the three isomers shall be analysed and their sum shall be reported (ΣHBCD(3)). It shall benoted that the total of the HBCD isomers can be analysed with GC-MS methods and can be reported as $\Sigma HBCD_{total}$)

For the reporting of the **toxic equivalent (TEQ)** (for PCDD, PCDF, and dl-PCB) it is recommended to report the concentrations of all 29 congeners and separately show the TEQ derived from PCDD, PCDF and dl-PCB as well as the total TEQ. According to the text of the Stockholm Convention (Annex C), the toxicity equivalency factors (TEF) as established by a WHO Expert Group and published in 1998 (WHO_{1998}-TEFs) should be used. However, state-of-the-art presentastion of results uses the WHO_{2005}-TEFs (Van den Berg et al., 2006) and therefore, it is recommended to report these as well in order to allow comparison with data from the literature and other reports.

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

For all sum parameters, the upper-bound (ND=LOQ) and the lower-bound (ND=0) values should be given. As a QA/QC measures, the difference between these two should be less than 20%.

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

3 STATISTICAL CONSIDERATIONS

The aim of this chapter is to review the statistical requisites that must be satisfied if a monitoring programme is to meet the objectives set out in Chapter 1. However, objectives at that level will not help to answer questions such as: *How many samples are needed for a robust result? For how long is continued monitoring needed? How frequently should be samples collected?* The risks of reaching the wrong conclusions (e.g. to conclude that there is a trend when there is not or to miss a true trend) have also to be considered.

3.1 Quantitative objectives

Describing and carefully defining the objectives are the most crucial steps in planning and organizing monitoring activities. It includes the choice of sampling matrices and rigorous definitions of sampling units and a description of what they represent in time and space. This description is a prerequisite for an appropriate interpretation of the results. In order to properly estimate, for example, the number of samples per sampling occasion, length of the time-series, sampling frequency etc., required for the investigation, qualitative and quantitative objectives in means of clear statistical hypotheses have to be defined.

A qualitative objective for temporal studies could be stated as follows:

> To detect a decrease within a time period of 10 years with a statistical power of 80% at a significance level of 5%.

A quantitative objective for temporal studies could be stated as follows:

> To detect a 50 % decrease within a time period of 10 years with a statistical power of 80 % at a significance level of 5 %. (A 50 % decrease within a time period of 10 years corresponds to an annual decrease of about 7 %).

A significance level of 5% means that there is a 5% probability to reach an erroneous conclusion about trends. Similarly, a power of 80% means that we accept a risk of 20% to conclude that there is no trend or difference when it really is one. Statistical power and methods to estimate power are discussed in detail in Cohen (1988).

In case of temporal trends, the qualitative objective should precede the quantitative objective, i.e. the trend should be identified first (at a given significance level) and if it is present, it should be quantified in the second step. It had to be stressed, however, that statistically significant trends do not guarantee that detected temporal trends are a result of a causal relation between concentration and time. If the samples are biased, not comparable over time or if relevant confounding co-variants are not accounted for, “false-trends” may well occur.

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

3.2 Statistical methods to be used

Both the classical (parametric) and more robust (but with smaller statistical power) non-parametric methods of trend assessment are used for the statistical analysis. Experience from the first two rounds of POPs data collection in 2008 and 2014 show that concentration values reveal biases from normality and follow a rather right-tailed statistical distributions, requiring use of the logarithmic transformation. Linear trend estimates (analysis of variance = ANOVA and simple linear regression = SLR) applied on aggregated log-transformed data provide information on achieving both the qualitative (significance of the change/trend) and quantitative (half-time of the compound, or annual increase/decrease in %) objectives, nevertheless they have several prerequisites - at least a normality of model residuals (i.e. no extreme or outlier values).

Data pre-processing

The correct definition of data is a prerequisite for the subsequent statistical analysis. Only reliably reported concentration values can be accepted for any spatial or temporal comparison. Therefore, a multilevel evaluation procedure based on the annually aggregated concentration values is proposed in order to maintain a high predictive value of the GMP records while avoiding bias in the concentration values.

Experience from the evaluation of the previous GMP data collection stages revealed a number of challenges related to data standardization, such as the lack of a standardized taxonomy for the listed POPs, their isomers, transformation products and summations. Some records provided detailed primary data, including rarely measured compounds, while others contained only the sums of the key groups of POPs. The heterogeneity of the data was further enhanced by reporting various toxic equivalents (TEQ) (based on the WHO TEF values from various years) rather than concentrations of the individual PCDDs, PCDFs and PCB congeners. Unclear identification of matrices, units, time scales of reported concentrations, as well as insufficient specification of aggregated data have also been identified. Large volumes of valuable data have been generated in all regions through the first GMP reports, and further standardization of reporting formats would significantly improve their applicability. A more elaborated guidance for handling, reporting and analyzing/interpreting these data will thus improve their applicability and support the development of the second GMP reports.

This experience described above led to establishment of data handling rules for the future data collection campaigns. These rules define mandatory data fields which correspond to the standardized data structure: typology of the background site; definition of the sampled matrix; taxonomy of parameters; sampling frequency (and data aggregation, if applied); measured value defined by its unit and variability (as further shown in chapter 6 regarding data structure).

The proposed data evaluation procedure for data processing guarantees comparability of the different samples, especially regarding the type of site, matrix, sampling method, time span and sampling frequency. Heterogeneity in the above information might dramatically increase the uncertainty in the final outcomes. The pre-processing procedures also limit the impact of uncontrolled covariates and thus reduce the risk of false trend detection or neglecting truly significant changes.

Initial data filtering stratifies the records according to the objective entities, such as site-matrix type and analyzed compounds. The filters must also check/verify the completeness of the primary database records in the reported sampling frequency, number of detected LOQs and their handling rules.

In the statistical part, the validation procedure excludes obvious extreme or unreliable values from quantitative analyses. The outlying concentrations can be identified by checking their quantile position in the sample distribution function. Estimated mean and standard deviation of log transformed annually aggregated data can be used for the reconstruction of the normal or log-normal distribution; a resulting pattern can be used to assess probabilistic position of the point values.

From primary to aggregated POPs concentrations

The most important source of variability in the atmospheric and water concentrations of POPs is their seasonal dynamics. This is not the case for human tissue data. Provided that primary concentration data sets are available, the impact of seasonality can be quantified and extracted from the time series (proper smoothing techniques, adjusting statistical models). Seasonally-adjusted time series constitute a base for the subsequent trend detection and quantification.

Annually aggregated data can also be used for spatial and temporal comparisons and quantification of time-related trends. In the first two GMP collection campaign reports, most records were annually aggregated arithmetic means. Considering an approximately log-normal distribution of primary data, the median value should be used for 3rd and any future GMP data collection campaigns rather than the arithmetic mean. Moreover, the aggregated values should be reported with appropriate variability estimates generated from primary data (minimum-maximum and/or 5th-95th percentile range are recommended). The quantity of non-detects (below LOQ values) in the primary records and their handling in the median calculations should be reported as well.

Statistical testing and its power

Power analysis is an obligatory step to define the magnitude of changes reliably detectable by the statistical methods. Power analysis minimizes the risk of misinterpretation or incorrect generalization of

the observed values. If necessary, the power calculation should be applied for both the statistical trend detection (SLR or Mann-Kendall test) and quantification (SLR or Theil-Sen estimator). The following two approaches are recommended for GMP data testing, especially for the time trend detection:

- Quantification of the minimum detectable difference between the annually aggregated values allowing to benchmark the identified changes against the statistically detectable levels;
- Prospective calculation of the sample size needed for the detection of a given relative time change in the POPs concentrations (e.g. 20% annual decrease).

Information on other statistical methods is also provided in AMAP (2014) and AMAP (2016).

Exploratory and confirmatory statistics: estimates and comparisons

Simplicity and robustness are the main principles when processing the GMP records. If assumptions of simple linear regressions are not met, non-parametric tests and summary statistics without or with negligible assumptions for the distribution patterns are highly recommended:

- For primary data: median estimates supplied with a 5th-95th percentile range are recommended for the annual aggregation;
- For annually aggregated values:Mann-Kendall test and Theil-Sen linear estimator (on log-transformed data)are recommended for comparative analyses in case when the assumption of SLR is not met (normality of residuals could be tested by Shapiro-Wilk test).

3.3 Sources of variation

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

Seasonal variation for several POPs (e.g. PCBs, PCDDs/PCDFs, DDTs and HCB) has been demonstrated. The reasons could be due to a seasonal variation in the discharge pattern from the sources, partitioning between different phases and, for example, physiological factors. If the main objective is to monitor the mean change in pollution load rather than to investigate the seasonal pattern in the discharges, sampling could be restricted to one season (the most favourable season from a minimum random variation point of view) or. better an annual aggregation of multiple samples should be applied in order to gain statistical power.

For ambient air, strong seasonal variations occur especially in temperate climate (e.g. Holt et al., 2017). The variation is caused by changing weather conditions, intensity of primary emission sources and revolatilization from secondary sources (e.g. higher concentrations of OCPs in summer due to more intense revolatilization and agricultural activity). This means that statistical evaluations sensitive to seasonal fluctuations cannot be performed directly on data sampled for a period shorter than one year. An aggregation of the values in every year is necessary to achieve values not influenced by the seasonal variation (Kalina, 2017).

It is relevant to use several summary statistics for the annual aggregation such as minimum, maximum, arithmetic and geometric mean and median function, which can be used for further assessment of the trends. Although the arithmetic mean was recommended by previous versions of the guidance document, experiences from the first two collection campaigns show significant biases from a normal distribution of concentration data. Based on this knowledge, rather the median should be used as a robust and simple statistic for the annual aggregation.

To obtain representative aggregated value for a given year, it is necessary to use data covering the whole year (continuous monitoring covering the whole year or samples covering regularly all significant seasons – at least four samples for sites with temperate climate). If the initial and final year of the time series are not fully covered with the sampling, they should be excluded prior the aggregation to avoid a bias.

There is a lack of experience with the seasonality of POPs concentration in water, nevertheless the results of the first two collection campaigns show that the differences between summer and winer samples are lower compared to that of the ambient air. The difference is usually below the factor of two, enabling to take one or two samples per year without limiting representativeness of the monitoring. Considering passive water samplers, integrating the concentration for several months, one or two samples per year should be the sufficient sampling frequency.

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

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

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

Although several more precise options are discussed by Helsel (2005, 2006), the most robust method for treatment of values below LOQ is their substitution by a constant value. This method is independent of the number of samples and the substituted value does not change when a new value is added to the dataset (this is the biggest disadvantage of all the most likelihood, imputation and Kaplan–Meier methods). The values below LOQ should be replaced by one half of the quantification limit prior their annual aggregation and the information of the portion of these values should be stored together with the aggregated value.

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

3.4 Length of time-series

It can be shown that several well-established monitoring programmes have surprisingly low power to detect temporal changes of significant importance (Nicholson and Fryer, 1991; Bignert et al., 2004). It is naïve to expect monitoring time-series of POPs to reveal changes with any confidence within a sampling period of five years unless the changes are very large. More likely, we would expect a period of at least 10-15 years to detect significant changes of moderate size (5% /year). The relation between the number of years required detecting trends of various magnitudes and the Coefficient of Variation at a requested power of 80% for the standard linear regression is displayed in Figure 3.1 below.

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

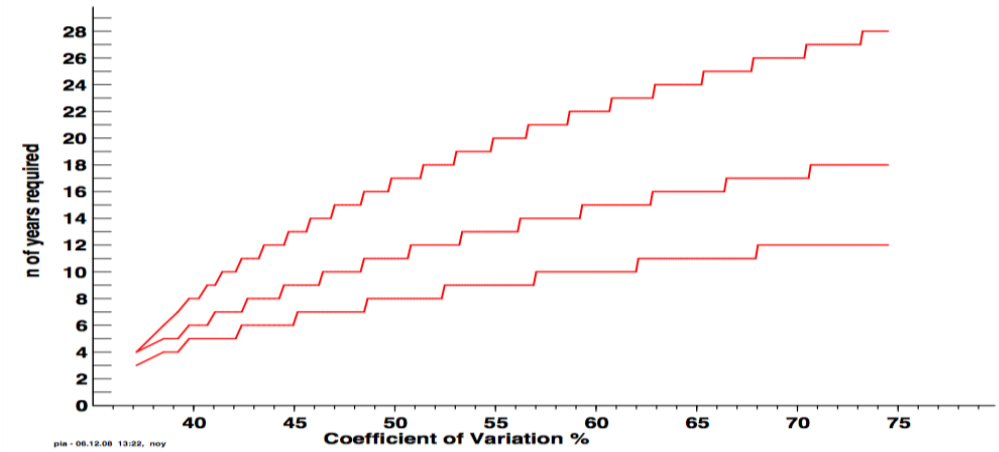


Figure 3.1: Number of years required to detect a 5 (left/above), 10 and 20% change per year respectively, at a power of 80% at a significant level of 5% applying a simple two-sided regression analysis for various magnitudes of between-years variation expressed as Coefficient of Variation (%) assuming single annual mean concentrations (or one pooled sample per year).

3.5 Number of samples needed

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

To estimate the number of samples needed for quantitative objectives, information on expected variance must be available (see above). The number of samples needed is even higher in case of non-parametric statistics. Based on experience from the first two POPs monitoring collection campaigns, the most frequent sample set size for identification of a trend (typically a decrease of POPs concentration) is between 7 and 10 years.

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

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

Additional information is provided in the relevant monitoring guidance from EMEP/EBAS, OSPAR, HELCOM.[4]

[4] OSPAR: Guidance for the Comprehensive Atmospheric Monitoring Programme (CAMP) - http://mcc.jrc.ec.europa.eu/documents/OSPAR/Guidance_fortheComprehensiveAtmosphericMonitoringProgramme_CAMP%20.pdf, EMEP/EBAS: http:\\ebas- submit.nilu.no, and HELCOM: http://www.helcom.fi/helcom-at-work/publications/manuals-and-guidelines.

3.6 Outcomes of statistical processing

The following outcomes are proposed for the statistical processing of GMP data:

- Summary statistics of atmospheric concentrations of POPs based on annually aggregated values;
- Parameters of the annual aggregation (number of values, numbers of values below LOQ etc.);
- Identification of a trend (its statistical significance);
- Quantification of the trend, and its size in form of a half-life and/or percentage of the annual change (increase or decrease).

Summary statistics of atmospheric concentrations of POPs

Annually aggregated POPs concentrations, calculated as medians of the primary values can be used for both quantitative and qualitative analyses. The overall arithmetic mean and median should be computed over the aggregated values, serving as a baseline estimation of a representative value for each site, as well as 5th-95th percentile range and min-max range as an estimation of variance. The delta statistic defined as a difference between the final and initial year can provide a simple insight into the trend characteristics.

Uncertainty analysis

As data reported to the GMP are typically generated by a variety of programmes, at several background sites of each UN region, they have to be inspected for an intra-regional and inter-regional homogeneity in the annually averaged POPs concentrations. Graphically, regional variability can be reported as the intra-regional 5th-95th percentile range. Sample distribution functions of the regional samples can then be compared and tested by proper robust methods (Shapiro-Wilk test or Kolmogorov-Smirnov test, Kruskal-Wallis test). The same applies for the geometric means of the averaged concentrations and their 95% confidence intervals.

The uncertainty analysis identifies regions or data subsets with increased intra-regional variability in the annually averaged concentrations and the sources of such variability (evident outlying values should be excluded). Any spatial or temporal comparison should be preceded by an assessment of internal homogeneity of concentration values in the areas of interest.

Similarly, the homogeneity should also be assessed in the time trend analysis (i.e. presence of and same direction in the trend change and annual difference). A year-to-year difference can be compared among time-series based on the individual sites. Such variability can be expressed as a standardized year-to-year difference or as a coefficient of variation (expressed in %). Applying time-related regression models and their residuals is possible as well. In accessible time series, homogeneity (or non-homogeneity) in a year-to-year variance indicates the degree of representativeness and stability of the identified time trends. The time series reported from various sites can be merged for more powerful trend analysis only if their homogeneity was proved.

Stochastic identification of time trends

Time trends are identified via a qualitative test of statistical significance of the time-related changes observed in the consecutive measurements. At least five consecutive annually aggregated concentration values are required when assessing time trends using one of the following robust techniques:

- Simple linear regression on log-transformed data fitted by least square regression technique accompanied by the F test of trend;
- The Mann-Kendall test, as a non-parametric test for detecting a trend in time series, based on binary coding of the changes in measurements consecutive in time.

The direction of the time trend (whether concentration values are increasing or decreasing in time) has to be recorded whenever it is confirmed as statistically significant. In addition, any concentration change over time should be reported in the same way, although there is no exact statistical significance behind it. Both statistically significant and non significant time changes over time must be correctly quantified in the reports and marked with the p value generated by appropriate tests (see 3.4).

Quantification of time trends

Quantification of time trends should be performed whenever the proper statistical tests confirm significant and consistent time-related differences in POPs concentrations. One of the linear regression techniques should be used on log-transformed annually aggregated data - simple linear regression (SLR) for datasets with the normal distribution and Theil-Sen non-parametric estimator (Theil, 1950 and Sen, 1968) for datasets without the normal distribution of the values, both providing an exponential trend. A quantified trend means a difference $\Delta=y1-y2$, where y1 and y2 correspond to annually aggregated concentration values recorded in two consecutive years. The time-related difference in the concentration value should be expressed with the following attributes:

- The relative annual change (%) expressed as an index of the value detected in the previous year;
- The half-life of the compound in the environment.

In addition to the evaluation of the temporal changes in POPs concentrations in core matrices, it can also be useful to monitor temporal changes of their relative contribution. Such information can provide new insights into the changing primary and secondary sources or the transport pathways of POPs.

3.7 Examples of statistical treatment and graphical presentation

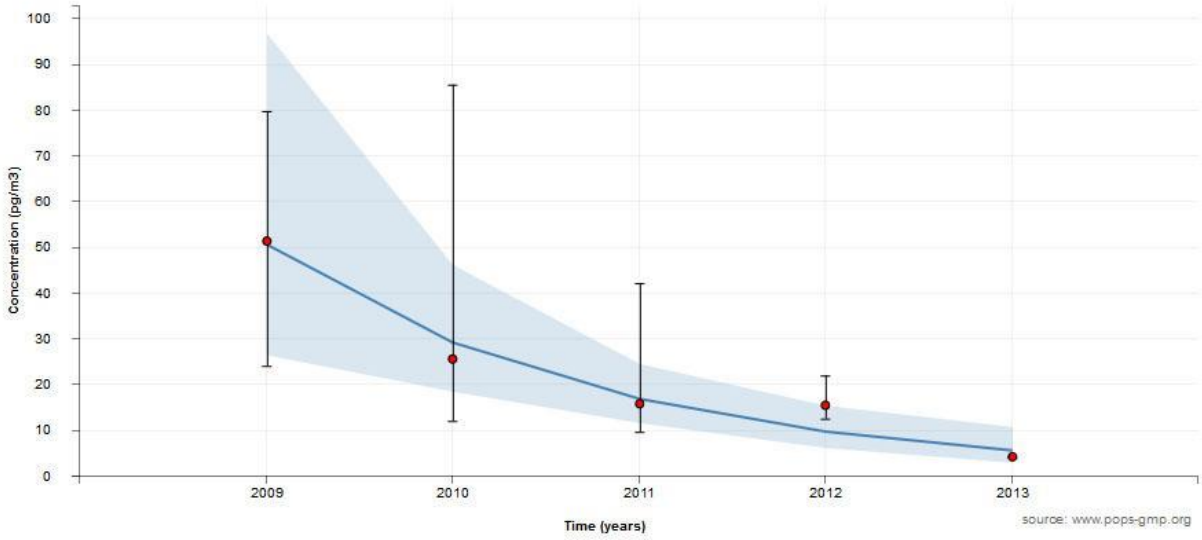
One of the main purposes of the monitoring programme is to identify temporal trends. Examples of methods to identify trends could be either the parametric simple log-linear regression (simple linear regression on log-transformed data) or the Mann-Kendall test (Gilbert, 1987, Helsel and Hirsch, 1995, Swertz, 1995) in case of data containing extreme values. Whereas the Mann-Kendall test of trend is more robust and versatile, it has a lower statistical power compared to SLR.

If the trend is identified (positive result of one of these tests, i.e. $p < 0.05$), a quantification of the trend should take a place to decide whether a quantitative objective is met. A linear regression on the log-transformed data should be carried out - either the SLR again or the Theil-Sen estimator in case of non-parametric data.

The slope of the line describes the yearly change in percent or expected half-life of the compound in the environment. A slope of 5 % implies that the concentration is halved in 14 years whereas 10 % corresponds to a similar reduction in 7 years and 2 % in 35 years.

In order to describe non-linear trend components in the development over time some kind of smoothed line could be applied. The smoother used in the example is a simple 3-point running mean smoother fitted to the annual geometric mean values. In cases where the regression line is badly fitted the smoothed line may offer a more appropriate description. The significance of this line is tested by means of an ANOVA (Analysis of Variance) where the variance explained by the smoother and by the regression line is compared with the total variance. This procedure is used at assessments at ICES and is described by Nicholson et al., 1995. An example of time series treatment is shown in Figure 3.2. below depicting a series from the GMP data warehouse.

Gamma-HCH on ERPC (Russia)



Download chart

Summary

Mean	22.477 pg/m3
Median	15.785 pg/m3
Minimum / maximum	4.1858 – 51.377 pg/m3
5th percentile / 95 percentile	6.4405 – 46.217 pg/m3

Trend description

Delta	-47.191 pg/m3
Exponential regression test	p = 0.012
Exponential regression half-life	1.23 year
Mann-Kendall test	-1 (p = 0.016667)
Theil-Sen half-life	1.23 year

Raw data

Search:

N	N Under LOQ	LOQ	Unit	Central Value	Central Value Type	Whisker Top Value	Whisker Bottom Value	Date
1	0	0.00	pg/m3	4.19	median	4.19	4.19	2013-01-01
3	0	0.00	pg/m3	15.46	median	21.99	12.54	2012-01-01
6	0	0.00	pg/m3	15.78	median	42.19	9.67	2011-01-01
9	0	0.21	pg/m3	25.58	median	85.63	12.05	2010-01-01
10	0	0.20	pg/m3	51.38	median	79.84	24.10	2009-01-01

Showing 1 to 5 of 5 entries

Figure 3.2: Examples of time-series; gamma -HCH levels measured at the ERPC site, Ufa, Russian Federation, measured between 2009-2013. The analysis is available in GMP data warehouse. The legend to the figure is found in Table 3.1.

Table 3.1: Legend to Figure 3.2

The plot displays the median concentration of each year (red circles) together with the 5%–95% percentile range (whiskers). The trend is presented by the blue regression line (plotted if Mann-Kendall $p < 0.05$). The log-linear regression lines fitted through the median concentrations follow an exponential function. Below the plot results from several statistical calculations are reported:
Mean, median, minimum/maximum, percentiles = summary statistics over the annually aggregated values (not the primary data). Five data points were used for these characteristics.
Delta = a simple difference between the initial and the final (aggregated) data point.
Exponential regression test = the p-value of an F test of the simple log-linear regression.
Exponential regression half-life = if the p-value is lower than 0.05, a half-life of the compound in the specific environment.
Mann-Kendall test = tau and the p-value of the Mann-Kendall test of trend.
Theil-Sen half-life = if the p-value is lower than 0.05, a half-life of the compound in the specific environment computed using Theil-Sen log-linear regression.
There are also some statistics describing the annual aggregation:
N= Total number of samples used for the annual aggregation.
N under LOQ = for each year of the monitoring, a number of samples which fall under a quantification limit.
LOQ = the level of the quantification limit.
Central value = the result of the annual aggregation. Should be only median in the 3rd and next collection campaigns.
Whisker bottom/top value = values of 5th and 95th percentiles of the annual aggregation.
e non-parametric Mann-Kendal trend test, and the corresponding p-value.
sd(sm)= The square root of the residual variance around the smoothed line. The significance of this line could be tested by means of an Analysis of Variance. The p-value is reported for this test. A significant result will indicate a non-linear trend component.

4 SAMPLING AND SAMPLING PREPARATION METHODOLOGY

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

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

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

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

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

4.1 Air

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

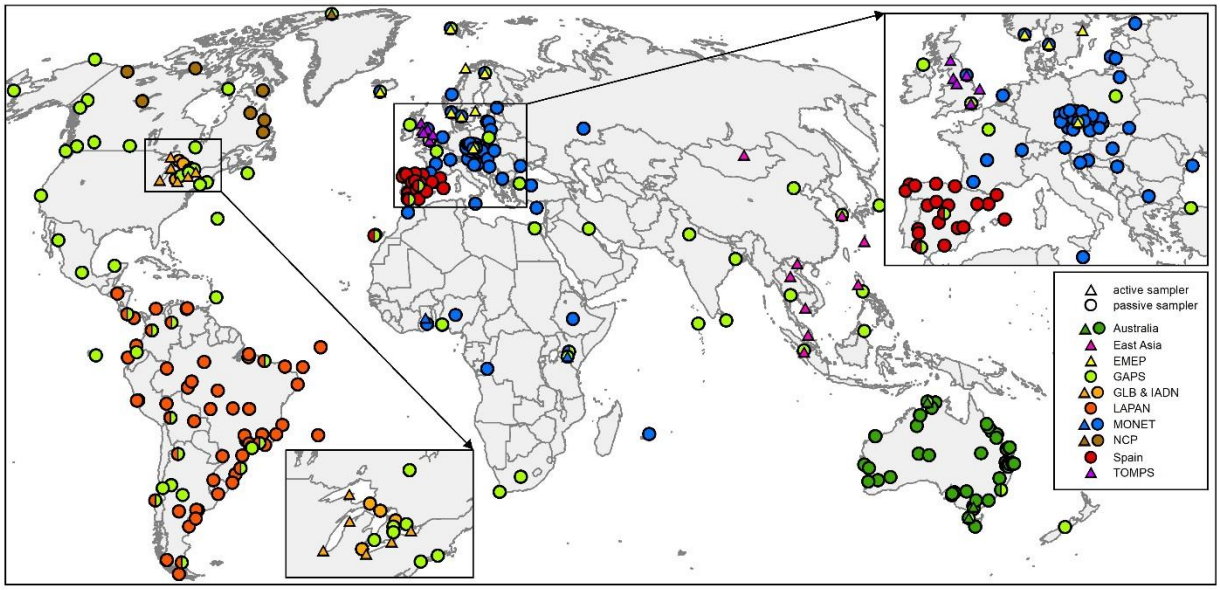


Figure 4.1.1: Sampling sites currently operating under existing active and passive air monitoring programmes for POPs that are contributing to the GMP. Site details are provided in Annex 2 Part I.

Several key recommendations stem from the 1st and 2nd global monitoring report and inform new and ongoing efforts to assess POPs in air for the purpose of effectiveness evaluation. These are summarized below and include, inter alia:

- A need to ensure internal consistency of data within programmes so that trends over time can be evaluated; at the same time, to strive for comparability of data among programmes so that data sets can be combined and made available through the GMP database;
- Laboratories in programmes contributing monitoring data to the GMP should participate in international interlaboratory assessments;
- The development of new and sustainable programmes for addressing data gaps for POPs in air should take advantage of partnerships with existing programmes; a specimen banking strategy should also be considered (i.e. collection and archiving of air samples for later analysis) if current analytical capacity is an issue;
- Additional funding and resources will be needed to respond to pressures for analysis of new POPs. In addition, monitoring programmes may need to adjust their protocols and resources to better align with new priorities. Some pressure can be relieved by reducing analysis frequency for legacy POPs (e.g. PCB, organochlorine pesticides) where declining trends have been established, optimizing analytical methods, and establishing partnerships among laboratories to address specialized analytical needs. It is not necessary for every laboratory to be an expert for every class of POPs;
- Monitoring of newly listed POPs in air should be undertaken as soon as possible so that adequate baselines are established;
- Acknowledgement that in some locations the response in air concentrations to control measures may be subject to a time lag due to the persistence of POPs;
- Strategies should be considered for making better connections between POPs monitoring and toxicity indicator tests for the assessment of long term, cumulative effects of chemical mixtures in the environment;
- Factors that determine concentrations of POPs in air, including changes in primary and secondary emission sources and climate effects must be considered, e.g. with the help of models, in order to properly interpret observed trends.

In addition to the guidance presented in this document we note that there are several other sources of information on best approaches and practices for measuring POPs and new priority chemicals in air such as, inter alia, the AMAP assessment reports (https://www.amap.no/documents/doc/AMAP-Assessment-2016-Chemicals-of-Emerging-Arctic-Concern/1624]). Furthermore, up to date methodologies for sample collection and data analysis are available in the peer review literature, which is especially useful for addressing specific technical and analytical challenges. Interested Parties seeking guidance should consider contacting these international experts directly.

4.1.1 Experimental design

Sampling sites

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

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

- One or more active high-volume air sampling stations which can provide episodic or cumulative sampling (for 1 to 2 days every week or continuously over periods of 1 to 2 weeks). These samples could be separated into particulate and gaseous fractions. We note that so far not all regions have a high volume station reporting to the GMP. This delay is most likely attributed to the higher costs and infrastructure required to operate these samplers;
- A network of 10 to 15 passive sampling stations, which provide continuous, cumulative passive (diffusive) sampling for integration periods ranging from a few months to 1 year. Co-location with high volume stations is useful for comparison purposes. We note that passive samplers continue to be established across all regions under the GMP resulting in greatly enhanced spatial resolution and information on POPs sources, transport and trends over time.

Examples of protocols, standard operating procedures and detailed guidance on air sampling, sample treatment and analysis are provided in Annex 2 Part II. Links to training videos are provided at the end of this chapter.

Siting considerations

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

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

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

- Regional representativity: A location free of local influences of POPs and other pollution sources such that air sampled is representative of a much larger region around the site;
- Minimal meso-scale meteorological circulation influences: Free of strong systematic diurnal variations in local circulation imposed by topography (e.g., up-slope/ down-slope mountain winds; coastal land breeze/lake breeze circulation);
- Long term stability: In many aspects including infrastructure, institutional commitment, land development in the surrounding area;
- Ancillary measurements: For the super-sites, other atmospheric composition measurements and meteorological wind speed, temperature and humidity and a measure of boundary layer stability. For the passive sites, meteorological wind speed, temperature and humidity;
- Appropriate infrastructure and utilities: Electrical power (for pumped samplers), accessibility, buildings, platforms, towers and roads, with care to avoid sources of potential contamination;
- Passive sampling sites should also take advantage of the freedom to deploy samplers well away from infrastructure (buildings, roads) and human activity which could be potential sources of POPs contamination.

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

Site type:	**Potential Source type (more than one type is possible):**
□ urban	□ industrial

□ sub-urban	□ traffic
□ rural	□ residential
□ remote	□ agricultural
□ high altitude	□ waste sector
□ polar	□ none, *i.e*. continental background site
□ marine/coastal	

Note: population density can be used as an approximate guide for site classification as follows:
urban = >200 000 inhabitants within a 10 km radius.
sub-urban = between 20 000 and 200 000 inhabitants within a 10 km radius
rural = between 2000 and 20 000 inhabitants within 10 km radius
remote = relatively uninhabited (<2000 inhabitants within a 10 km radius)

Site information and classification is important for comparing data within a region and among regions. Although new sampling networks should focus on sites that are representative of a large sub-region or 'footprint' (*i.e*., rural sites), the establishment of sites in urban, industrial, and agricultural regions may be useful as 'context sites' for comparison purposes. For regions that are relatively pristine for some POPs, the inclusion of context sites will also improve detection and reporting of POPs. Again, care should be taken to ensure that these 'context sites' are not directly or heavily influenced by just a few nearby point sources. So, for instance, a city park of university campus, could be 'representative' sites for urban air if they are located within the city limits and not dominantly impacted by nearby emissions sources of POPs.

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

Characterization of transport to the sites

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

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

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

Chemical	CTD in air, km	CTD in water, km	TE% (emission to air)
Hexachlorobenzene	230 000	700	2500
Hexachlorobutadiene (HCBD)[1]	160 000	100	50
Pentachlorobenzene	120 000	200	50
Octabrominated Diphenyl ethers	22 000	360	110
PCB-180 (hepta homolog)	17 000	340	91
α-HCH	7800	830	54
PCB-28 (tri homolog)	5100	190	2.2
Pentachloroanisole (PCA)[2]	4300	220	5.2
γ-HCH	4200	220	19
BDE-99	3700	540	15
DDT	3600	490	10
β-HCH	3100	430	3.7
Hexabromobiphenyl	3000	540	13
BDE-209	2900	120	13
Toxaphene	2800	1600	7.9
Short-chain chlorinated paraffins[1]	1800	230	0.78
2378-TCDD	1600	130	0.58
Dieldrin	1100	580	0.89
chlordanes	1100	300	0.46
chlordecone	710	1700	3.2
Aldrin	60	130	0.00018
PFOS**	10	63 000	0.049

TE – transfer efficiency for emissions to air; HCH – hexachlorocyclohexane; PCB-polychlorinated biphenyl; DDT – dichlorodiphenyltrichloroethane; TCDD – tetrachlorodibenzodioxin; PFOS – perfluorooctane sulfonate;
*Calculations using OECD Tool are summarized at: http://www.sust-chem.ethz.ch/docs/POP_Candidates_OECD_Tool.pdf http://www.pops.int/documents/meetings/poprc/prepdocs/annexEsubmissions/All%20chemicals%20Switzerland.pdf
**calculation of CTD for air for PFOS assumed no potential to volatilize to air.
[1] MacLeod et al., 2007; [2] Reppas-Chrysovitsinos et al., 2017.

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

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

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

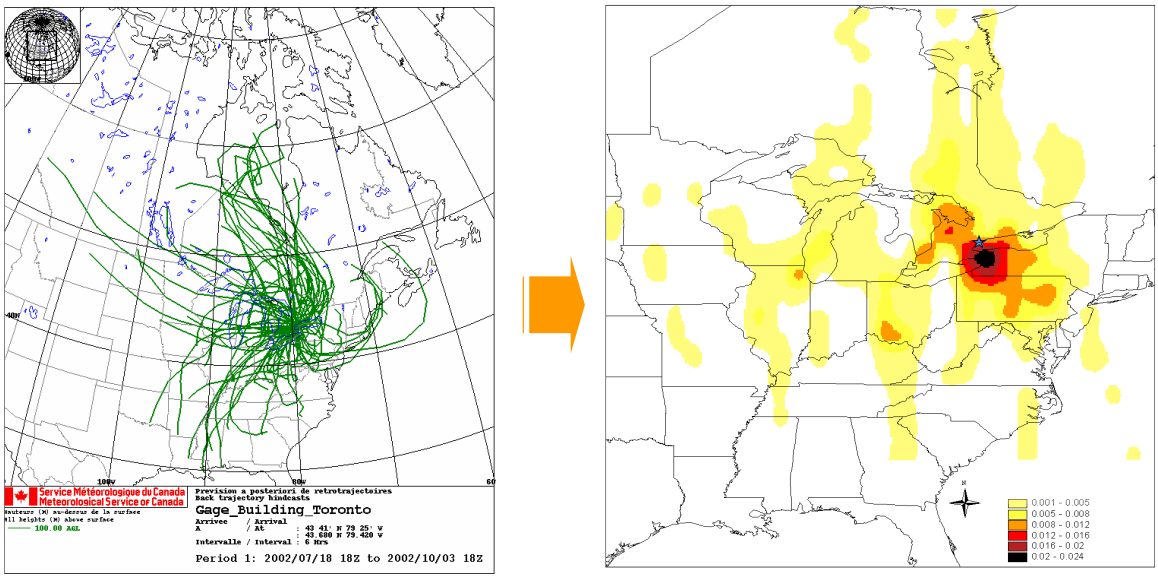


Figure 4.1.2: Example of probability density map (right panel) constructed from daily 3-day air parcel back trajectories for a time-integrated air sample (left panel). The darker shadings in the right panel indicate regions where air masses passed over a greater proportion of the time before arriving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

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

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

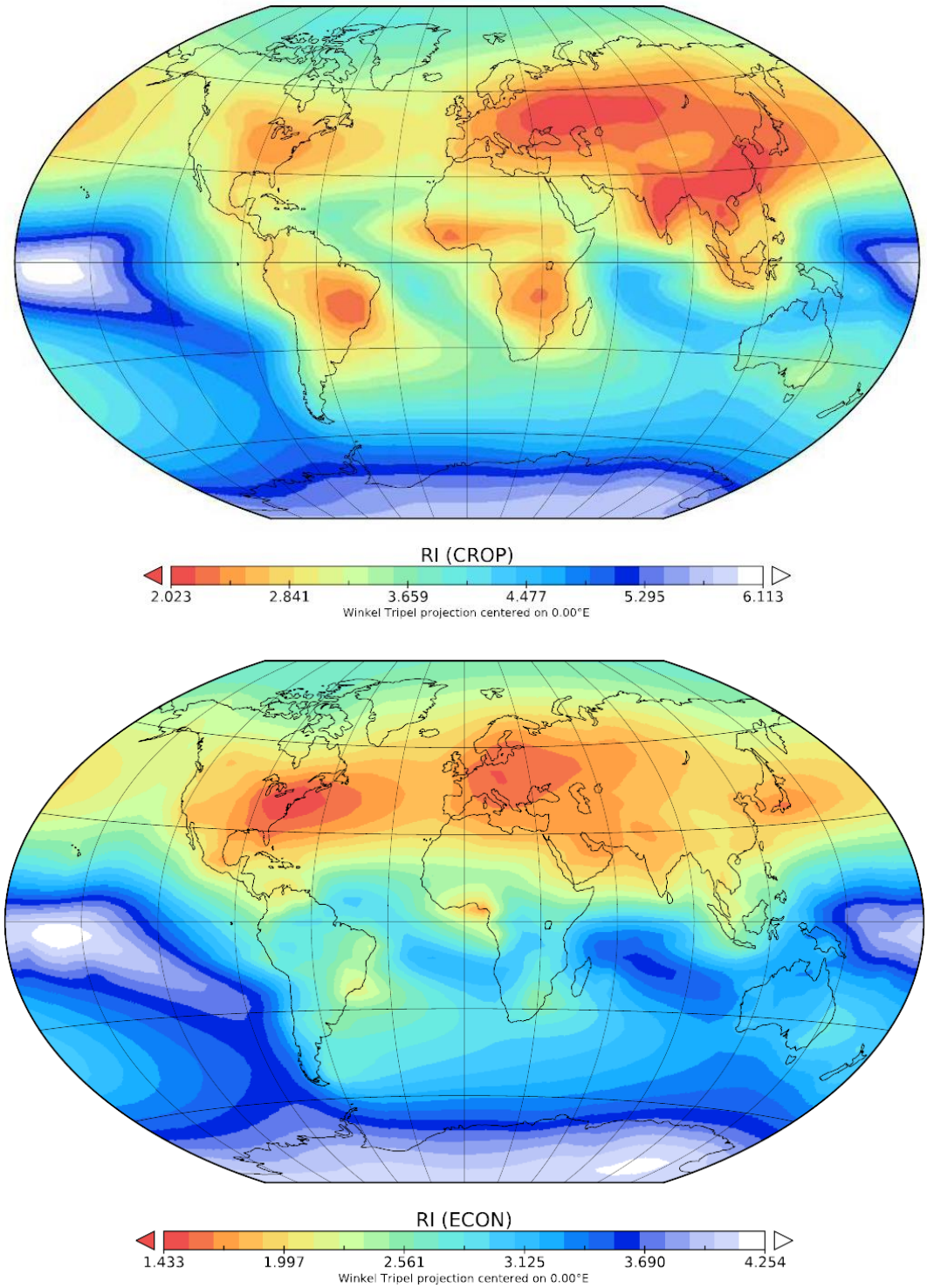


Figure 4.1.3: Global distribution of remoteness index for the CROP (top) and ECON (bottom) scenarios. CROP refers to pesticide emissions and ECON refers to technical emissions (von Waldow et al., 2010).

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

Northern Hemisphere, and transport from temperate regions to the Arctic is occurring. For example, models indicate that more than 50% of PCBs currently being deposited to the Great Lakes region of North America are attributable to distant emission sources.

Special considerations for newly listed POPs

PFOS: Any air monitoring strategy investigating the occurrence and/or long range transport of PFOS to remote regions should include PFOS derivatives and precursor compounds. The gas-phase transport of PFOS is limited because it is an ionizable chemical (Table 4.1.1) that partitions strongly to water and in the atmosphere will partition to aerosols. Sea salt spray aerosols are an important emissions source of PFOS and other perfluoroalkyl acids to air and this emission source should be considered for monitoring stations located near coastal areas (Johansson, J., 2017). The occurrence of PFOS at background and remote sites occurs through an atmospheric pathway mediated through the long-range transport of more volatile precursor chemicals that ultimately degrade to PFOS. Therefore, in order to understand the occurrence of PFOS at background sites, it is necessary that these derivatives/precursors be monitored in air.

This strategy is consistent with COP4 Decision SC:4/17 that lists perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride to Annex A and B of the Convention. The decision refers to the draft risk management evaluation report of the Persistent Organic Pollutants Review Committee (POPRC) [UNEP/POPRC.2/17/Add.5, UNEP/POPRC.3/20/Add.5 and UNEP/POPRC.4/15/Add.6.] which for regulatory purposes adopts the European Union (EU) definition of PFOS. Under this definition PFOS includes all molecules having the following molecular formula: C8F17SO2Y, where Y = OH, metal or other salt, halide, amide and other derivatives including polymers (European Union, 2006). Compounds targeted for air monitoring are listed in Chapter 2, Table 2.2.

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

HCBD, PCP (and related chemicals) and other volatile POPs: the relatively higher volatility of some POPs may present challenges for typical air sampling methods due to limited sorptive capacity of sampling matrices such as polyurethane foam (PUF) and even XAD-resin (Rauert et al., 2018b). Therefore, data should be interpreted accordingly and using the latest information and tools available. This topic is discussed further in section 4.1.3 on air sampling.

POPs used in commercial products and building materials: many of the newer classes of POPs (e.g. BDE-209, HBCD, SCCPs) experience widespread use in products that may results in off-gassing or other contamination pathways that ultimately may affect the integrity of the sample. Recognizing and avoiding potential contamination sources is essential in selecting appropriate sampling locations and during sample processing in the laboratory.

4.1.2 Sample Matrix

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

POPs Distribution in Air

Many POPs are semi-volatile chemicals that exist both freely dissolved in air and attached to particles. Their proportion on particles increases at lower temperatures due to a reduction in the chemical's volatility. The extent of partitioning onto particles will affect a chemical's fate and transport in the environment, since large particles (e.g. greater than 10 μm) and fugitive dusts have high deposition velocities and tend to deposit from air close to where they are emitted, typically within several kms (Lin et al., 1994); gaseous compounds may or may not be subject to relatively high deposition velocities

depending on their reactivity in air, whereas fine particles tend to experience lowest deposition velocities and, consequently, longest transport distances in air (Giorgi, 1988). Inhalation of fine particles is an important exposure pathway for some classes of POPs that can contribute to health impacts (Degrendele et al., 2014). Particle-association may also enhance the persistence of POPs and protect them from atmospheric degradation reactions and, thereby, increase their potential for long range transport in air (Liu et al., 2014). Atmospheric fate of particle-associated POPs is an area of ongoing study.

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

Active air samplers (Fig. 4.1.4) typically include a pre-filter for capturing particles. This filter can then be extracted and analysed separately. However, the ability to accurately measure the particle-phase component is confounded by blow-off/on (sorption artifacts) (Melymuk et al. 2014; Bidleman and Harner, 2000) and degradation/stability of collected chemicals (Jariyasopit et al., 2015). The breakthrough of fine particles through the filter is another artifact that may lead to overestimation of the gas-phase component. Denuder samplers, in which the gas-phase is collected first, followed by the particle-phase, is an alternative method for overcoming these limitations and artifacts (Lane, 1999). However, denuders are currently not capable of the higher volume flow rates of conventional high volume samplers, so longer sampling times are often required to detect trace levels of air contaminants.

The PUF disk sampler (Fig. 4.1.5) has been shown to collect both gas-phase and particle-phase POPs (Harner et al., 2014) with similar efficiencies as for typical high volume air samplers (Markovic et al., 2015). This is largely due to the sampler housing design that allows ambient particles to enter the sampling chamber and porous properties of PUF that capture and entrain deposited particles. Different sampler types (both active and passive) may have different particle sampling efficiencies. Therefore, it is important that within a program the same sampler housings designs are used at each station to ensure comparability among sites and over time. It should be noted that many other passive air samplers types (PE films, XAD sampler) target mainly gas-phase chemicals.

4.1.3 Sampling and sample handling

Air sampling requires the following capacities: (1) active and passive air samplers, (2) trained station personnel to operate and maintain the high-volume samplers, (3) meticulous preparation of clean sampling media in the laboratories performing the extraction procedures and chemical analysis. Sampling methods and QA/QC procedures should, as far as possible, be adopted from existing air monitoring programmes for POPs, but they will need to be adapted to and validated for the specific conditions, concentration levels and temperature at the sampling sites. High volume and passive sampling approaches are detailed below. Other sampling strategies are envisioned that may produce comparable data for national and regional reporting and these should also be considered. Some indirect approaches such as sampling vegetation (biomonitoring) and deposition and the use of tree rings Odabasi et al., 2015; Rauert et al. 2017) to explore historic trends are valuable parameters for assessing environmental loadings. However, care must be exercised when trying to use these data to infer air concentration trends quantitatively.

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

High volume sampling

Networks that employ high volume air samplers to measure atmospheric POPs are summarized in Fig. 4.1.1. In almost all cases these networks employ sampling heads with size-selective inlets for collecting particles below some cut-off size threshold, typically particles smaller than 10 micrometers diameter. Sampling should take place using techniques practiced by routine long term monitoring networks in temperate and cold environments (*e.g.* Fellin et al., 1996; Environment Canada, 1994) and sub-tropical to tropical regions (*e.g.* Ministry of the Environment of Japan and the National Institute for Environmental Studies). These groups recommend the technique of separating particles from gases using the combination of glass fibre filters in series with two gas absorbents. The nature of the type of absorbents used need to be matched to the needs of the regional monitoring programme and target analytes (e.g. PUF, XAD, XAD-PUF, activated carbon felt). A schematic of a generic high volume system is shown in Fig. 4.1.4 and samplers are available from numerous suppliers.

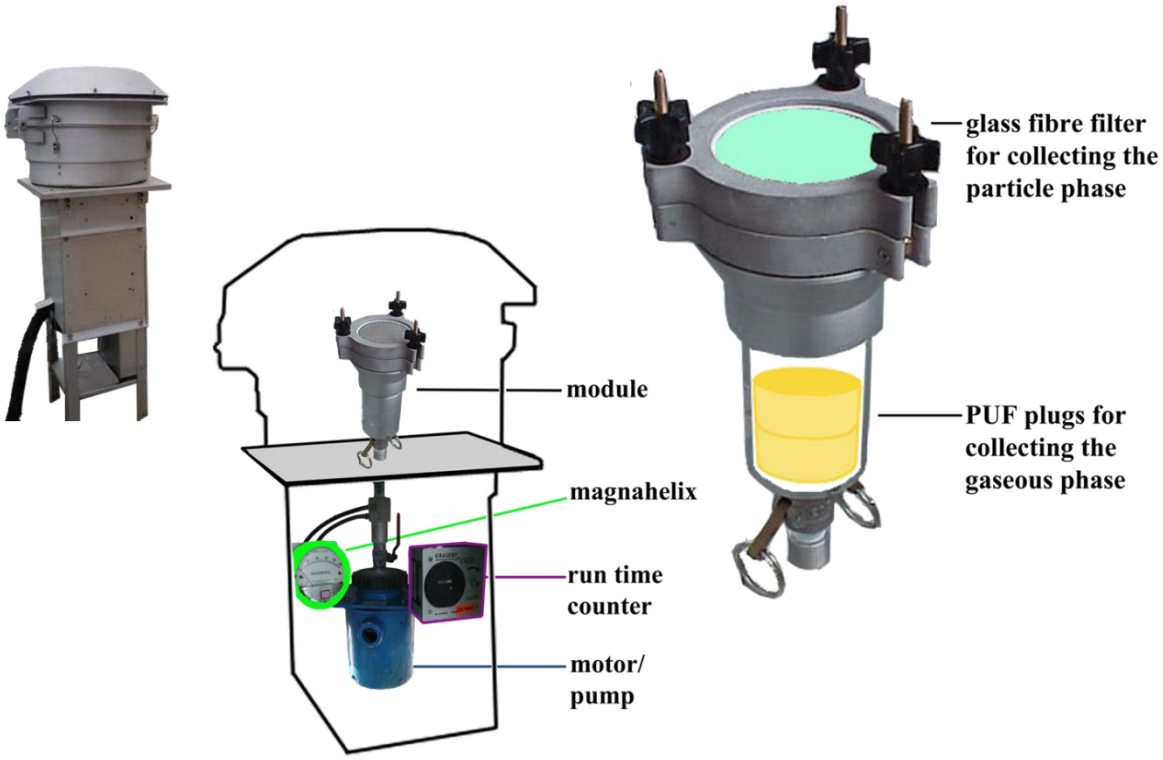


Figure 4.1.4: Schematic of typical active air sampler (high volume air sampler). Note particle collection substrates typically include glass fiber filters (GFF) or quartz filters; whereas typical gas-phase sorbents include PUF and XAD-resin or combination of the two.

Several possibilities exist which are favoured for long term measurements and should be selected by experienced experts planning a regional study:

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

For the gas-phase,

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

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

The sampling schedule is also an important design consideration that will partly depend on available budget. Samples could be taken intermittently (*e.g*. approximately once every week or every 2 weeks) or continuously (weekly integrated) with care taken to minimise analyte breakthrough. Breakthrough can be minimized by using a higher capacity sorbent for the gas-phase collection or a reduced air sample volume. Breakthrough is reduced at cold ambient air temperatures when the sorptive capacity of the sampling matrix is increased. As a rule of thumb, the sorptive capacity of the sampling matrix (e.g. PUF plug) will increase by a factor of about 3 for every 10 ºC decrease in air temperature. Recommendations for dealing with air sampling breakthrough are presented in Bidleman et al., 2018.

Field blanks should be taken every several samples. Field blanks are treated in the same manner as samples including placement in the sampler housing, except no air is drawn through them. In some cases air is drawn through the field blank but only for a very short period of time (*e.g*. seconds to minutes). The method detection limit (MDL) is often based on the levels of target analytes in blanks, rather than by the sensitivity of the analytical instrument (see section 4.1.4).

Absorbents are pre-cleaned prior to sampling. Filters are usually pre-treated by baking at high temperatures. Samples should be put into the sampling head using environment and handling practices that are free of contamination and volatilization losses. Many POPs are semi-volatile and may evaporate from sampling media if they are warmed appreciably above ambient temperatures. After sampling, samples and field blanks are extracted in the appropriate solvent (e.g. hexane and dichloromethane are common). Although Soxhlet extraction is a commonly used extraction method, other extraction techniques such as accelerated solvent extraction, microwave extraction and sonnication are also used, depending on the target compounds. Extracts are concentrated prior to analysis and it is a common practice to archive some portion. This allows samples to be re-analyzed years later when analytical techniques may have improved and there is new information (such as on additional POPs) to be gained. Specimen banking is discussed further in Chapter 8.

Passive sampling

There are several centralized passive air sampling networks contributing internally consistent, regional-scale and global-scale information on POPs to the global monitoring plan and targeting new priority chemicals in air. As a result of their low cost and simplicity the adoption of passive air sampling for addressing data gaps and for assessing spatial trends and long-range transport of POPs has accelerated greatly since the first GMP report. Interested researchers are encouraged to refer to research papers and on-line information for up-to-date information on these programs, including GMP data available on the GMP database (http://www.pops-gmp.org/) and GENASIS (http://www.genasis.cz/index-en.php). Some of the key passive air sampling networks contributing to the GMP are outlined briefly below:

1. GAPS Network (https://twitter.com/GAPSNetworkPOPs) **(**https://www.canada.ca/en/environment-climate-change/services/air-pollution/monitoring-networks-data/global-atmospheric-passive-sampling.html**):** The Global Atmospheric Passive Sampling (GAPS) Network has been operating since 2002 as a pilot phase at 7 sites and then starting in 2005 at more than 50 sites. It now includes more than 60 sites on all 7 continents. At all sites PUF disks samplers (Fig. 4.1.5) are deployed quarterly. Sorbent impregnated PUF (SIP) disks (Fig. 4.1.7) are deployed every second year since 2009 to detect volatile POPs. Yearly deployment of XAD-samplers is also included at a subset of about 20 sites. Key publications include: Harner et al., 2006; Pozo et al., 2006, 2009, 2011; Genualdi et al., 2010; Shunthirasingham et al., 2010; Koblizkova et al., 2012; Schuster et al., 2015; Eng et al., 2016; Rauert et al., 2016, 2018),

2. MONET (http://monet.recetox.muni.cz/index-en.php?pg=localities--europe)**:** The MOnitoring NETworks (MONET) spinned off the EMEP central European air monitoring supersite in Kosetice where the PUF-PAS (passive air samplers) are continuously co-employed with the high volume samplers since 2003 providing important calibration and validation data. In the beginning it was focused on filling the air monitoring data gaps in central and eastern Europe (high resolution pilot studies starting 2004), Asia and Africa (starting 2008), currently it includes numerous sites in Africa, Asia and Europe complementing the high-volume air monitoring efforts within the EMEP network. Long-term data with monthly/quarterly resolution are available via GENASIS data warehouse (www.genasis.cz). Key publications include Zencak et al., 2007; Klanova et al., 2007,

2008, 2009; Adu-Kumi et al., 2012; Pribylova et al., 2012; Lammel et al., 2013; Holt et al., 2017; Kalina et al., 2017).

3. LAPAN: The Latin American Passive Atmospheric Sampling Network (LAPAN) has been operating since 2010, as a pilot project initially at 6 countries, and gradually has increased the number of sites and participant countries. It now comprises about 70 sites along 13 countries from the GRULAC (Group of Latin America and Caribbean Countries) region. At all sites, XAD-based samplers (Fig. 4.1.7) are deployed annually (Wania et al., 2003). At least 6 sites have LAPAN XAD-based PAS deployed side-by-side with PUF-based samplers from GAPS.

4. UNEP-GEF Projects (http://web.unep.org/chemicalsandwaste/what-we-do/science-and-knowledge/persistent-organic-pollutants-pops/pops-monitoring, http://web.unep.org/chemicalsandwaste/what-we-do/science-and-risk): UNEP-GEF projects (Fiedler et al., 2013) have been implemented since 2005 and presently are scheduled until 2020. Unlike the long-term monitoring programs described above, the GEF project generates unique data in the context of capacity building and training. In total, 45 developing countries have participated in capacity building activities including with an emphasis on sampling the core matrices of the GMP and on-site training of developing country laboratories in POPs analysis. The data from air monitoring with PUF passive air samplers exposed for three months have been analysed by three training laboratories and were reported by the national coordinators into the GMP warehouse ((Bogdal et al., 2013; Fiedler et al., 2014; Fiedler et al., 2013; Lal et al., 2013; Martrat et al., 2012)). Presently, two-year sampling and capacity building projects are underway in three UN regions including 42 countries. In a few countries, the suitability or need for amending the PAS network with active samplers is being tested.

The PUF disk sampler (Fig. 4.1.5) is the most widely used air sampler under the GMP and also in research studies to investigate the levels and long-range transport of POPs and priority chemicals in air. Because of the widespread use of the sampler, it has also been evaluated in numerous independent studies (Herkert et al., 2018; Kalina et al, 2017, Holt et al, 2017, Bohlin et al., 2014; Harner et al., 2014) and recently in an international intercalibration described below.

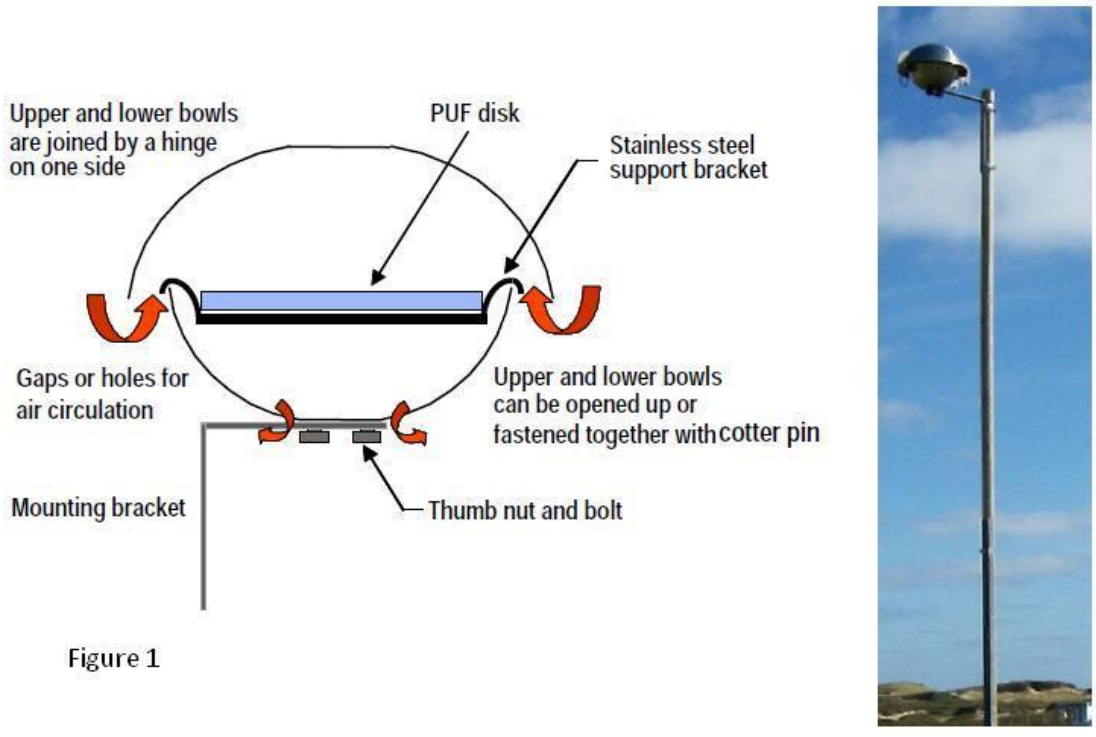


Figure 4.1.5: Schematic of PUF disk passive air sampler.

Comparability of PUF disk samplers: An international intercomparison exercise for PUF disks samplers, including 15 laboratories, was carried out in 2016-2017 led by the Norwegian Institute for Air Research (NILU), in collaboration with the Research Centre for Toxic Compounds in the Environment (RECETOX) and Environment and Climate Change Canada (ECCC) (Bohlin et al., in prep.). The study

revealed a few discrepancies in results for POPs among research groups when participants performed their own analysis, with each group providing their own sampler housing (Fig. 4.1.6 (top)); whereas the results were much more consistent and comparable when all the analysis was performed by a reference lab (Fig. 4.1.6 (bottom)), using the sampling chambers and PUF disks provided by each group. The results highlight the advantages of using a central laboratory for regional and even global-scale programs.

The PUF disk sampler collects both gas-phase and particle-phase chemicals (Markovic et al., 2015; Harner et al., 2013, 2014). The sampling rate is sufficiently high e.g. 4 ± 2 m^3/day that quarterly resolution (and in some cases monthly resolution) is possible, although typically PUF disks are deployed for 2-3 month periods.

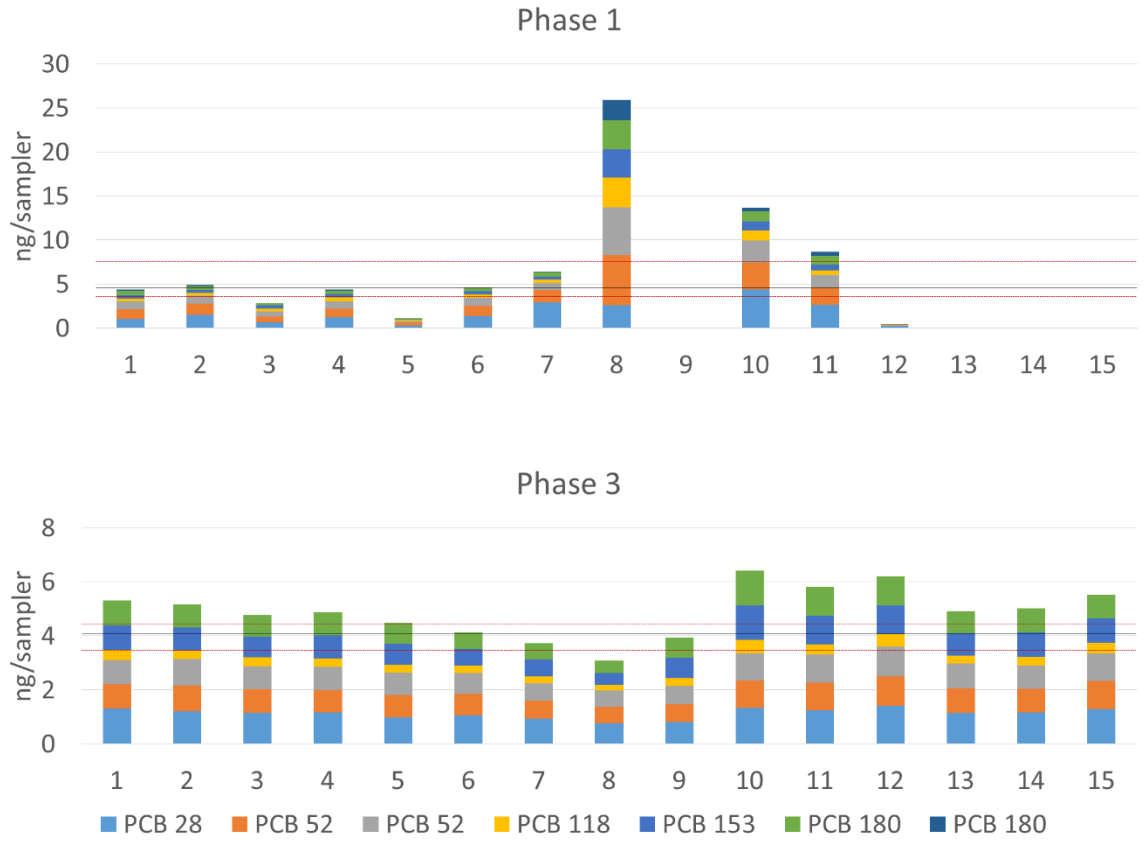


Figure 4.1.6: Results from international intercalibration study of PUF disk samplers for PCBs. In top panel samples were analyzed by individual labs while in bottom panel all samples were analyzed in a central lab (RECETOX). Several PUF disk sampler chamber types were used, including GAPS-type, MONET-type and CSIC-type among others.

This is in contrast to the XAD type passive air sampler used in LAPAN and in a subset of GAPS sites, which targets mainly gas-phase chemicals (Fig. 4.1.7). Because of its lower sampling rate (~0.5 m^3/day) but high sorptive capacity, the XAD sampler is typically deployed for yearly resolution (Gawor, et al., 2013). In some cases annual sampling may be sufficient – especially if informational on seasonality of POPs in air is not required and if the main objective is to determine long-term trends (Hayward et al., 2010).

The sorbent impregnated PUF disk i.e. SIP disk sampler (Fig. 4.1.7) is similar to the XAD sampler in the sense that it allows for greater sorptive capacity of the PUF disk. This allows it to meet challenges associated with the more volatile POPs e.g. HCB and polyfluoroalkyl compounds (Rauert et al., 2018). However, the porous PUF substrate of the SIP disk also ensures that low volatility POPs associated with particles in air are captured and entrained. Comparison of PUF and SIP disk samplers have shown good comparability and demonstrate the complementary nature of the two sampler types (Genualdi et al., 2010). These comparisons include PCBs (Genualdi et al., 2010) and OCPs (Koblizkova et al., 2012), PFOS, its precursors (*e.g.* MeFOSE, EtFOSE, see Chapter 2, table 2.2), fluorotelomer alcohols and other perfluoroalkyl compounds (Genualdi et al., 2010; Rauert et al., 2018), volatile methyl siloxanes (Genualdi et al., 2011; Rauert et al., 2018) and penta- and hexachlorobenzene (Koblizkova et al, 2012). Field

calibration of SIP disks has also demonstrated their potential application in longer time-integrated sampling of legacy POPs (*i.e*. longer than the conventional 3-month sampling used for PUF disks) (Schuster et al., 2012). Comparison of XAD and PUF disk samplers have also shown good comparability of the two sampler types for gas-phase compounds (Hayward et al., 2010).

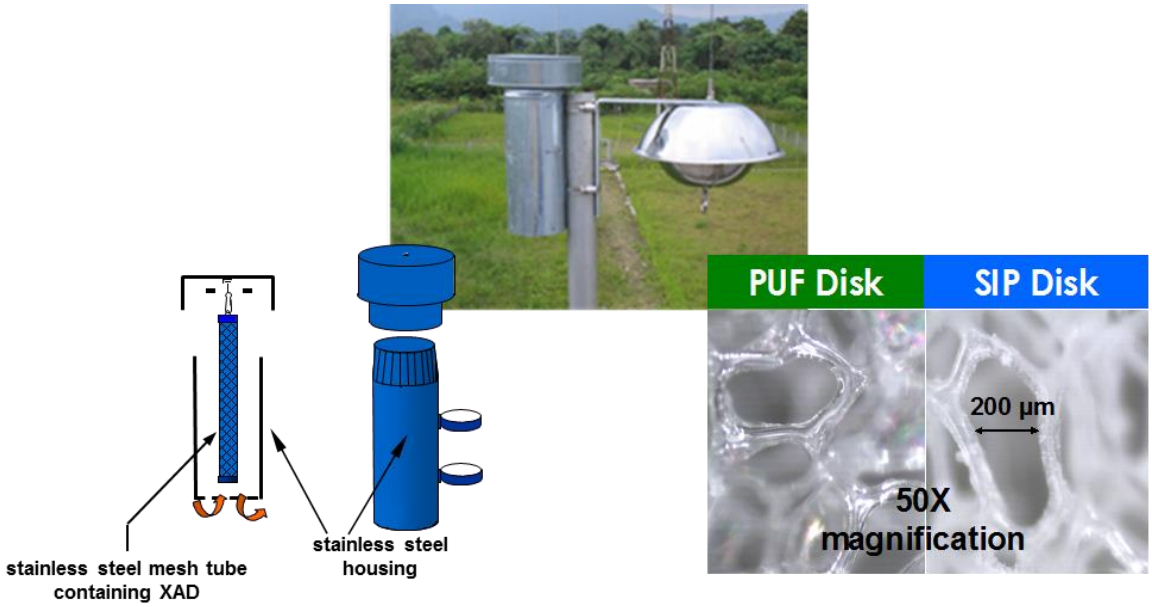


Figure: 4.1.7: High capacity passive air samplers for targeting volatile POPs including XAD-sampler (gas-phase) and SIP disk sampler (gas + particle phase). Magnification of PUF disk and SIP disks showing porous structure of polyurethane foam and coating of ground XAD powder on SIP disks.

Deriving concentrations in air for POPs in PUF (and SIP) disk samplers: Sampling rates, R-values, for PUF-disk based samplers are typically on the order of ~4 ± 2 m3/day (Pozo et al., 2006, 2009; Harner et al., 2014) and so a 3-month deployment provides an equivalent sample air volume of approximately 360 m3, which is sufficient for the detection of most POPs in ambient air. Shorter integration periods of 1 month have also been incorporated successfully (e.g. Holt et al., 2017). The wind-effect on sampling rate for the domed chamber design has been evaluated under controlled conditions (Tuduri et al., 2006), from field study results (Pozo et al., 2004; Klanova et al., 2006) and using flow simulation models (Thomas et al., 2006). Generally, the chamber is capable of dampening the wind-effect on sampling rate by maintaining the air flow within the chamber at less than ~1 m/s. However, higher sampling rates have been observed at windy, coastal and mountain sites (Pozo et al., 2004, 2006, 2009).

Herkert et al., (2018) have recently reported on a global-scale model able to derive site-specific sampling rates and effective air sample volumes for POPs collected using PUF disk samplers. This is an improvement over the use of default sampling rates as it accounts for site-specific variability. The model [http://s-iihr41.iihr.uiowa.edu/pufpas_model/] only requires lat/long information for the sampling location and the time period for the deployment. The model then retrieves meteorological data assigned to these coordinates (wind speed, temperature) to calculate R for any location in the world (see Fig. 4.1.8). The model also accounts for approach to equilibrium in PUF disk for more volatiles POPs (discussed below). Model agreement with sampling rates derived using depuration compound (DCs, see below) was shown to be good for gas-phase compounds. Sampling rates for particle-associated POPs are expected to be similar but may vary depending on shelter configuration (Markovic et al., 2015).

A more precise but more complex measure of the air volume sampled may be achieved by spiking the sorbent prior to exposure with known quantities of “depuration compounds” or DCs. These are isotopically-labelled chemicals or native compounds that do not exist in the atmosphere and cover a wide range of volatility (assessed based on their vapour pressure and/or octanol-air partition coefficient, Koa). The loss of depuration compounds over the sampling period is used to calculate the effective air sample volume (Pozo et al., 2004, 2006, 2009; Persoon and Hornbuckle, 2009). The air concentration is then calculated based on this air volume and the amount of chemical collected over the sampling period. An

on-line tool is available for deriving effective air sample volumes for a wide-range POPs for both SIP disk and PUF disk samplers (Harner et al., 2017).

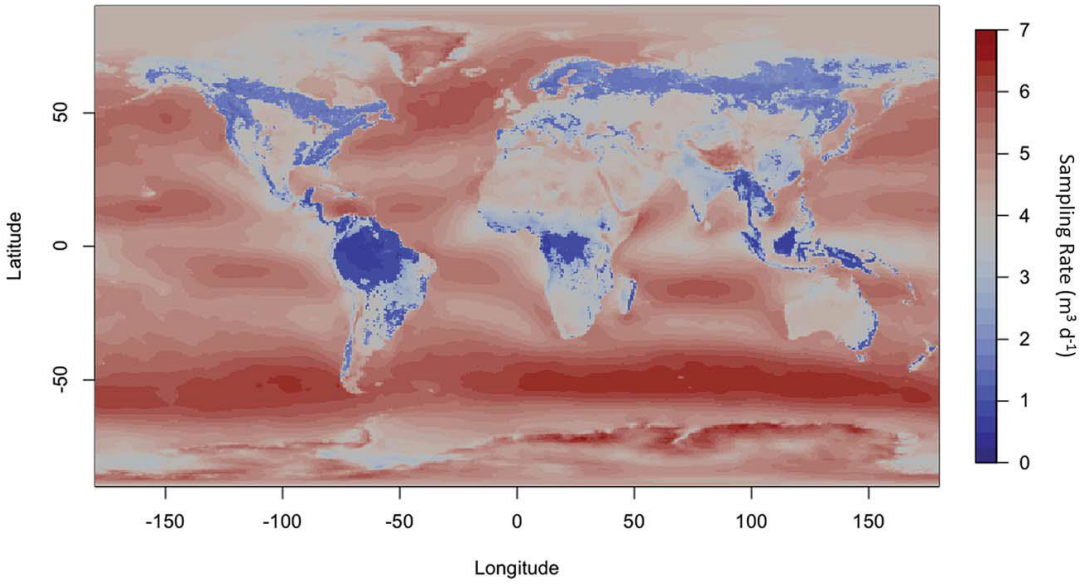


Figure 4.1.8: Annual mean PUF-PAS sampling rate (m^3 d^{-1}) of a tri-chlorinated PCB congener in 2006.

Approach to Equilibrium and Equilibrium sampling: It is imperative to account for approach to equilibrium that may occur for the more volatile POPs (*e.g.* HCB, Pentachlorobenzene, HCBD, etc) (Harner et al., 2004; Gouin et al., 2005; Pozo et al., 2006). Approach to equilibrium results in a gradual reduction in the sampling rate until the net rate goes to zero at equilibrium. For the most volatile compounds that do reach equilibrium over typical PUF disk deployment periods of a few months, the effective air sample volume is dependent on $K_{puf\text{-}air}$ and not R. In some ways, this is not a disadvantage as $K_{puf\text{-}air}$ can be estimated accurately and even measured easily directly (Parnis et al., 2016; Francisco et al., 2017) and does not vary with windspeed. Using PUF disk as equilibrium samplers can result in improved accuracy of derived air concentrations. However, if approach to equilibrium is achieved too quickly e.g. hrs to a few days then this is not ideal since the resulting concentration in air will only reflect ambient concentrations during the last few days of deployment. This would not be a concern however, for chemicals with relatively constant ambient air concentrations over period of weeks to months, which is typical of volatile POPs (e.g. HCB) at background sites.

Sampling and sample preparation: Prior to use PUF disks are pre-cleaned by sequential extraction (Soxhlet or accelerated solvent extraction) using a combination of polar and non-polar solvents (*e.g.* acetone: hexane and/or acetone followed by hexane; and toluene is typically used for dioxin analysis). It is important that PUF are extracted with the same solvents used in the precleaning stage, to help ensure good blank levels. Samples are stored in solvent-rinsed and gas-tight glass jars or solvent-rinsed aluminium sleeves within airtight containers (e.g. freezer bags). One field blank should be deployed at each site to assess potential contamination. These field blanks are typically inserted to the sampling chamber, removed immediately and then stored and treated as a sample. Samples are extracted using the same techniques as for active air samples described above. Similarly, analysis of extracts follows procedures outlined in Chapter 5.

Further considerations regarding air sampling, including toxicological assessment for chemicals mixture in air, use of tree rings and other natural archives for deriving historic trends of POPs, and sampling of indoor air are included in Annex 2, Part III.

4.1.4 QA/QC and Data Treatment

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

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

An extensive review and assessment of quality assurance activities under the Integrated Atmospheric Deposition Network (IADN) is present in Wu et al. (2009). QA/QC and data treatment procedures that are used under the international AMAP air program are presented in Fellin et al. (1996) and updated in Hung et al. (2010, 2016). QA/QC protocols for several international air monitoring programs are included in Annex 5.

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

QA/QC considerations

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

Blanks:

- Method or lab blanks – This is usually done by using a clean matrix and/or solvent and treating as a sample, taking it through the entire methodology in order to assess contamination. It is useful to run method blanks prior to starting a campaign to ensure the integrity of the methodology. Method blanks are particularly important for some of the newly listed POPs (PBDEs, PFOS and related compounds) which may be elevated in the laboratory environment. If contamination is an issue, blank test could be performed on different stages of the methodology to determine and isolate the source of contamination. Method blanks should be run routinely during processing of real samples, at least one blank for every 10 samples (i.e., 10%).
- Field blanks - These are sample media (*e.g.* PUF disk, GFF, XAD, etc.) that are installed in the sampler and removed right away and then stored and treated as samples. Field blanks account for additional sources of contamination that may arise due to sample handling, transport and storage. Care should also be paid to avoid other potential sources of contamination that may arise from the sampler itself or nearby sources. For instances flame retardants or other substances (*e.g.* chlorinated paraffins and its impurities (Takasuga et al., 2012) that are used in electrical equipment or construction materials (*e.g.* PCBs in sealants).

Sampling Efficiency / Sampling rates:

- Breakthrough check – In the case of high volume samplers, a second sorption matrix is placed in series to the first to assess breakthrough of gas-phase analytes through first matrix (*e.g.* PUF plugs, PUF/XAD cartridges). Breakthrough is particularly important for more volatile compounds. Some of the newly listed POPs such as PeCBz, HCB, and a-HCH are known to exhibit substantial breakthrough on PUF due to their volatility. Volatility and breakthrough increase at warmer temperatures (Melymuk et al., 2016; Bidleman et al., 2018).
- Adsorption artifact – In the case of high volume samplers, some gas-phase compounds may sorb to glass- or quartz fiber filters which are intended to capture particle-phase compounds. For analysis procedures that treat gas- and particle-phases separately, this will result in overestimation of particle-phase partitioning. This artifact can be assessed by using a second filter in series with the first and analyzing the two filters separately. Ionic compounds such as PFOS have been shown to have a substantial adsorption artifact (Arp and Goss, 2008). Note that Teflon filters should be avoided when targeting PFOS and related chemicals.

Recoveries and use of surrogates:

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

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

Detection:

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

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

- Instrument Detection Limit (IDL) and dealing with data that falls below the IDL – The instrument detection limit is determined from the amount of analyte that will produce a signal:noise of 3:1 on the analytical instrument. This can be estimated by extrapolation of the result for the lowest concentration standard. The IDL value is compound specific and will also vary from day to day according to instrument performance and sensitivity.
- Limit of Quantification (LOQ) - The LOQ convention is rarely used in trace air analysis with the exception of analysis of dioxins and furans. LOQ is typically defined as 3 times IDL or 10 times the signal: noise. These two conventions result in similar numbers.

Data treatment - Qualifying data, blank and recovery correction:

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

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

- Qualified raw data and blank-corrected data (i.e. raw data that has exceeded the MDL and was then blank corrected). The mean blank values and MDLs for each analyte should be specified;
- Recovery-corrected data should only be reported when internal surrogates were used for each sample. Otherwise, results should not be recovery-corrected and external recovery values should accompany the data for assessing the methodology (data quality).

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

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

Data comparability

The issue of data comparability applies in several ways:

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

The derivation of temporal trends of POPs in air is critical for assessing effectiveness of control measures on POPs. This requires that a data set for a given program is internally consistent. Internal consistency can be achieved by adapting strict sampling protocols and laboratory QA/QC practices as discussed above to ensure that data are not influenced by factors other than real changes in air concentrations. Some of the long-term monitoring programs are often required to continue to use original analytical techniques that may be currently 'out-of-date', in order to ensure that contemporary data are consistent with samples analyzed ten or even twenty years ago. Any significant changes to the methodology should be accompanied by an intercomparison strategy to assess and quantify and correct for divergence (e.g. Su et al., 2011).

Although less critical for effectiveness evaluation, inter-program comparability is useful for investigations of regional and global transport of POPs and in the context of model application and evaluation. Inter-program comparability can be assessed through intercalibration exercises that should ideally address variability caused by using different sampling techniques, equipment, and media, as well as variability of analytical results and data handling. Several comprehensive international interlaboratory compasisons have been completed and reported in the last decade: Su and Hung (2010) indicated that in general, interlaboratory differences of up to a factor of 2 can be expected but that intralaboratory precision was generally good with relative standard deviations typically <10%. Within the UNEP-GEF projects, three rounds of interlaboratory assessments have been concluded, the fourth is underway presently (2018/2019) (de Boer et al., 2008; Fiedler et al., 2017; UNEP, 2012, 2015). Since the 2nd round in 2012/2013, air extracts have been included as test matrices to allow POPs laboratories to assess their performance for this core matrix and the POPs recommended for analysis (for analytes, see chapter 2). Whereas in the 2nd round, the performance for the air extract was poorer than in other matrices, in the third round overall quite good results were obtained. However, it needs to be highlighted that extracts have been provided so that the labs did not have to undertake clean-up and extraction of the PUFs. Among the POPs groups, best performance was for PBDE and dioxin-like POPs with 71% and 69% of all results "satisfactory"; poorest performance was for the broad group of organochlorine pesticides where about half of the results submitted were "not satisfactory" (49% were satisfactory). For toxaphene and HBCD the number of laboratories submitting results was too low and the results too scattered so that no consensus values could be determined for the three HBCD and the three toxaphene congeners.

As described in section 4.1.3, the first intercomparison exercise for passive samplers (PUF disk) was recently completed and included 15 international labs. The results indicated that variability attributed to the various PUF-PAS designs was low; whereas variability attributed to analytical differences among lab was significant in some cases. However, there is good agreement between the major networks delivering PUF disk-derived data for the GMP.

Another strategy for assessing and improving inter-program comparability is by setting-up master stations that include overlap between two or more sampling programs. In this way, sources of variability beyond just laboratory variability can be assessed. Some overlap of monitoring network sites is already occurring and could be exploited to evaluate this issue. Data comparability in a broader sense also comes into play

when reporting data from different sampling approaches (e.g., passive vs active; gas-phase, particle-phase or total concentrations) and strategies (e.g., time-integrated sampling or intermittent sampling such as 1 day in 10). A one-year field intercalibration study by Dreyer et al. (2010) demonstrated good comparability between high volume and SIP disk samplers for the polyfluorinated compounds. Even longer term comparisons of PUF disks and high volume air samplers have been established for several POPs classes at the Kosetice site in the Czech Republic. Holt et al. (2017) have explored the comparison of PUF-disk and active air sampler data from long term data at Kosetice and found that on an annual basis, the results for most POPs were within the same order of magnitude. Kalina et al., (2017) have also demonstrated good comparability between PUF-PAS and active high volume sampling for yearly aggregated data spanning several years as shown in Figure 4.1.9. Melymuk et al (2017) have investigated the impacts of degradation of POPs within the air samplers by reactive atmospheric gases, and found that while less persistent compounds such as polycyclic aromatic hydrocarbons may be susceptible to within-sampler degradation, the effect on evaluated POPs (PCBs, DDT, HCHs, PBDEs) is minimal, and should not significantly affect comparability between different sampler configurations.

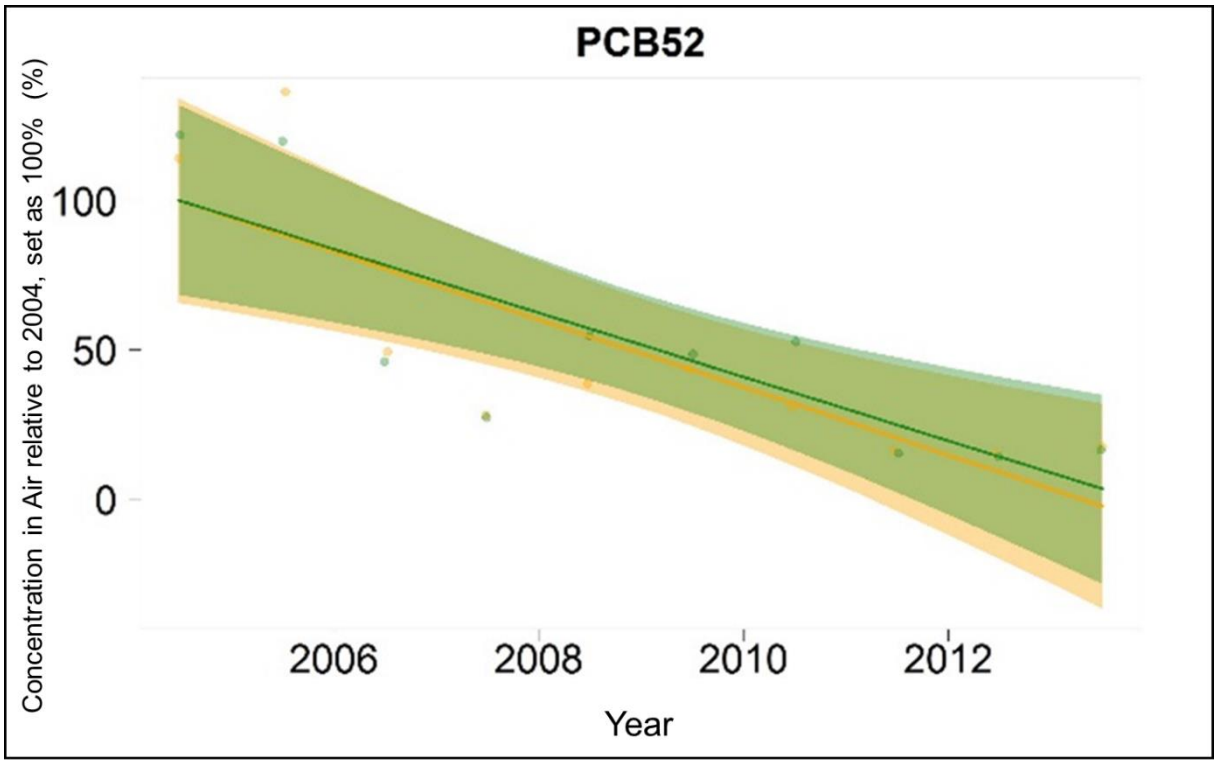


Figure 4.1.9: Linear model plot from Kalina et al. (2017) for PCB-52 covering the period 2004 to 2013 at Kosetice, Czech Republic using data acquired under MONET **(passive)** and EMEP **(active)**. The model is scaled relative to 2004 which represents 100% of the air concentration and is based on annually aggregated data, trend line, and 95% confidence intervals.

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

To summarize, a large amount of supplementary information is required for interpreting and comparing data, especially between programs. Efforts to handle and summarize these data would be greatly facilitated if the primary data were reported according to the guidance provided in this document. In most cases, air concentrations should be reported in units of concentrations (typically pg/m^3) and include details on how the sample was collected, what the sample represents (gas- vs particle phase) and a description of the location (site category) (see section 4.1.1). In some cases, it may be necessary to normalize sample concentrations to standard temperature and pressure to correct for variability in sample air volumes due to pressure and temperature extremes *e.g.* for high altitude or extremely cold sites, in cases where the samplers are not designed and calibrated to adjust automatically (Fellin e al., 1996). Some passive sampling studies have reported results in units of mass per sample due to uncertainty in the effective air

sample volume. In this case, it is important that the data be normalized to the duration of the sample (*i.e.* on a per day, per month or per year basis as appropriate) to improve comparability of reported data.

4.1.5 Climate Effects

The topic of climate change and its impact on contaminant pathways introduces even more complexity for temporal trend data analysis (Macdonald et al., 2005; Ma et al, 2011, 2016). Correlations between air concentrations of POPs and low-frequency climate variations (*e.g.* North Atlantic Oscillation - NAO, El Nino-Southern Oscillation (ENSO) and the Pacific North American (PNA) pattern) have already been demonstrated (Ma et al., 2004). This is of special concern in regions such as the Arctic where expected temperature increases and associated geophysical cycles are maximized (Macdonald et al., 2005). In addition to temperature increases, other meteorological disruptions associated with climate change (*e.g.* increased floods, droughts) may affect POPs mobility and air concentrations trends.

All of these topics should be considered when interpreting trends. Because of the site specific nature of these processes, (e.g., PCB-52 in Fig. 4.1.10) it is important that trends be considered on a site-by-site basis rather than implying regional coverage with the given number of sites. This strategy will also help to ensure comparability of data.

The issue of climate change on POPs was recently addressed by an AMAP/UNEP expert group to address the mandate given to the Global Coordination Group (at COP4) to assess climate influences on the levels of POPs measured in the environment and in humans and how these influences may interfere with present and future evaluations of the effectiveness of the Stockholm Convention measures (UNEP, 2011). Several recent reviews and studies also explored the impact of climate and associated direct and indirect changes and the environmental cycling of POPs (Armitage et al., 2011; Pacyna et al, 2015; Zhao et al., 2015, 2017; Ma et al., 2016).

Key messages that relate to climate influences on POPs in air include:

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

4.1.6 Integration

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

Recycling and re-emission from waste streams (e.g. landfills) are important factors for these time lags as they impact the emission profiles of newer POPs that are used in commercial products Shunthirasingham et al., 2018; Rauert et al., 2018b).

Informed decisions regarding the fate and behaviour of POPs requires an integration of information on chemical properties, emissions, models results and monitoring data (Fig. 4.1.10). This integrated approach is also an iterative process in which one type of information may inform the other and lead to re-evaluation. For instance, spatially resolved monitoring data may allow the application of new types of models. Discrepancies between model results and measurements may lead to a review of estimated emission scenarios.

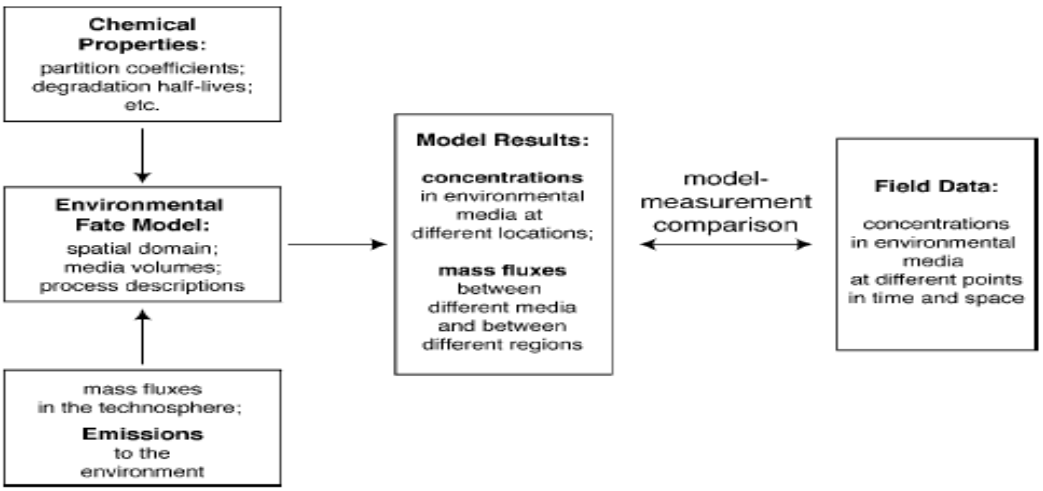


Figure 4.1.10: Integrated information required to make informed decisions on the environmental fate of a chemical (Scheringer, 2009).

4.2 Human milk and human blood

4.2.1 Experimental design

The objective of human monitoring within the GMP is to identify temporal and, as appropriate, spatial trends in levels of POPs in humans. The programme also assists regional capacity building in developing countries by supporting technical/analytical capability to detect regional trends of POPs in humans. Furthermore, by comparison of levels of POPs found in a statistically reliable number of representative samples from a certain country with levels found in such samples from other regions, priorities for a possible follow-up in a country with regard to a certain POP can be derived. This can be achieved very cost-effective, if a statistically reliable number of individual samples is collected and then aliquots are mixed to form a representative pooled sample which then is analysed by qualified reference laboratories for all relevant POPs (see details below).

Human milk and human blood have been used as markers of exposure of humans to a number of POPs for several decades and are core media for POPs biomonitoring under the Stockholm Convention. Both these sample media show comparable temporal trends in a particular population because they integrate environmental exposure as well as dietary exposure related to different consumption habits. Furthermore, they provide relevant information on POPs transfer to infants and potential health effects. To this end, only POPs concentrations in human milk and human maternal blood from first time mothers are considered comparable under the GMP (see details below).

Human milk

Comprehensive human milk monitoring programmes have been initiated by WHO. Early WHO surveys performed mainly in Europe and North America in 1987-1989 and 1992-1993 exclusively focused on PCB, PCDD and PCDF. In 2001-2003, a larger global survey was implemented, covering the twelve POP

compounds initially listed in the Stockholm Convention. Following the ratification of the Stockholm Convention, WHO and UNEP started their collaboration, and three additional global surveys were completed in 2004-2007, 2008-2011 and 2012-2015. These studies significantly enlarged the geographical scope providing representative results for all regions of the globe. A follow-up study started in 2016. This survey is ongoing and currently covers the 30 POPs listed in the Stockholm Convention.

Under WHO, a protocol has been developed for sampling and sample preparation methodology for exposure studies of Persistent Organic Pollutants (Malisch & Moy, 2006; WHO, 2007). This protocol forms the basis for the human milk component of the GMP (UNEP, 2017a). An online version of the protocol is available at http://www.who.int/foodsafety/chem/POPprotocol.pdf (see also Annex 3).

The main objectives of these studies are: 1) to produce reliable and comparable data on concentrations of POPs in human milk for further improvement of health risk assessment in infants, 2) to provide an overview of exposure levels in various countries and geographical areas and to allow to draw conclusions on priorities for further follow-up in a country / region, 3) to determine trends in exposure levels.

In order to promote reliability and comparability of results, samples are collected by the participating countries following a harmonized comprehensive protocol developed by WHO (WHO, 2007) and amended by UNEP (last amendment: see UNEP, 2017a). Participating countries are encouraged to adhere as closely as possible to the protocol, which provides guidance on the number and type of samples, selection of donors, collection, storage and pooling of samples, and shipping of samples to the reference laboratory. For all studies, the following criteria for selection of donating mothers are stringently applied:

- They should be first time mothers;
- They should be healthy;
- They should be exclusively breastfeeding one child (i.e., no twins).

In order to get statistically reliable data, an appropriate number of individual donors must be recruited to provide samples for the survey. As a first approximation, a minimum of 50 individual samples is recommended for each country. Equal aliquots of these individual samples are mixed to form a representative composite sample (“pooled sample”). The power of the survey can be increased by the inclusion of more than 50 individual samples and is encouraged. It is recommended to collect one representative individual sample per one million citizens. In particular, countries with populations greater than 50 million should include at least one additional participant per one million population over 50 million. Countries with populations well over 50 million (or with sufficient resources) are encouraged to prepare a second pooled sample (or more) if feasible.

The representative pooled sample is analysed for the 30 POPs listed in the Stockholm Convention by the reference laboratory. This approach has several advantages:

- The analysis of pooled human milk samples is also far less expensive than the analysis of all individual samples;
- It is easier for each donor to provide the lower volume of milk required for pooled analyses. Therefore, in comparison to analysis of individual samples, much more sample amount is available allowing a more comprehensive analysis with lower limits of quantification;
- To ensure the reliability of exposure data and to improve comparability of analytical results from different laboratories, a reference laboratory was selected based on inter-laboratory quality assessment studies. To further ensure consistency in measurements, all pooled samples are analyzed by the WHO/UNEP reference laboratories using validated methods;
- Aliquots of the individual samples can be analysed for analytes of interest by laboratories selected by the National Coordinator.

This combination of selection of a statistically reliable number of individual samples, preparation of a representative composite sample and analysis of the pooled sample for the 30 POPs listed in the Stockholm Convention by the reference laboratory is a very cost-effective way to derive information on the relevance of certain POPs in certain regions in humans as end-point of releases of POPs and to follow time trends.

QA/QC and comparability of the data in the frame of the programme is ensured by centralized analysis of the pooled sample. The State Institute for Chemical and Veterinary Analysis of Food (Germany) has met all the criteria for analyses of lipophilic POPs in human milk and was selected as a reference laboratory for the WHO exposure studies (WHO 2000, Malisch and van Leeuwen 2002, 2003). It is also the EU Reference Laboratory for halogenated persistent organic pollutants (POPs) in feed and food (COMMISSION REGULATION (EU) 2018/192). Proteinophilic POPs (e.g., PFOS) are analyzed at the MTM laboratory at the University of Orebro, Sweden.

Results of the WHO/UNEP Human Milk Survey for PCDDs, PCDFs, PCBs and DDTs were evaluated with particular focus on benefit–risk evaluation of breastfeeding (van den Berg, M. et al., 2017).

Human blood

To ensure comparable results across human matrices, human maternal blood is considered core medium under the GMP. Other type of donors can be considered in human monitoring programmes to generate information on concentrations of POPs over time, but they are not readily comparable with the human milk results and should be treated as other media.

Human maternal blood (plasma and serum) is used by AMAP as the prime matrix to determine human exposure (AMAP, 2009). Although it is an invasive procedure, in some cases it may be the matrix of choice, based on local infrastructure, customs and existing activities. As in the case for human milk, pooled samples can be used as a cost effective method for comparing POPs levels between and within countries and to elucidate time trends. Activities targeted at monitoring proteinophilic POPs such as PFOS are equally more likely to make use of blood as a preferred sampling medium. There seems to be a general trend that a growing proportion of hazardous compounds are more polar and may bind to proteins thus making blood the preferred medium in the future.

The Arctic Monitoring and Assessment Programme (AMAP) organized comprehensive human maternal blood plasma[5] monitoring with standardized protocols for specimen collection and analysis in the Arctic since the early 1990s. Maternal blood plasma, supplemented with some human milk data have been used in assessing PCBs, organochlorine pesticides and human health (AMAP 1998, 2002). In the last assessment, PBDEs and perfluorinated compounds were also included (AMAP, 2009).

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

AMAP has, in collaboration with Centre du Toxicologie de Quebec, developed a protocol for sampling and sample preparation methodology for exposure studies on POPs in human maternal blood. The protocol developed is the standard for all blood sampling procedures in AMAP. A detailed description of sampling, storage, shipping and analytical details is presented in Annex 4, but the protocol is also available online at www.amap.no. A number of laboratories have met the requirements set by the AMAP Human Health Expert Group and are thus providing data for maternal levels of POPs within the AMAP network. Through the AMAP network additional information like standardised questionnaires are available.

Long term human monitoring data obtained in the frame of the Arctic Monitoring and Assessment Programme are assessed in relation with and used to improve public health (AMAP 2015). These decades long efforts to use monitoring for public health in Canada, Greenland, Denmark, Sweden, Norway, Finland, Russia have provided interesting results and can be considered as a blueprint of future work in the next decades for other regions as well.

Blood concentrations accurately reflect the body burden of most contaminants, whether lipophilic, protein-bound, or ionic. For weakly lipophilic compounds, concentrations are much higher in blood than in milk. As an example, perfluorooctanesulfonate (PFOS) serum concentrations were found to be 100-fold greater than breast milk concentrations in paired maternal-newborn samples (Kärrman et al., 2007).

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

For lipophilic compounds, which include most POPs, blood concentrations expressed on a lipid basis are well-correlated with concentrations in other compartments such as stored fat and breast milk.

To enable such comparisons with human milk data at the global level, only human maternal blood from first time mothers is considered as a core medium under the GMP.

4.2.2 Sample matrix

There are three main tissues where the POP levels are normally measured: human maternal blood, cord blood and human milk. Several studies of the relationship between breast milk, maternal blood and cord blood levels of POPs have been carried out and shown correlation between the levels of lipophilic contaminants in these compartments to a certain degree, if lipid-adjusted (Jarrell et al. 2005 comparing maternal blood, cord blood and breast milk, Muckle et al. 2001 comparing cord and venous blood; Anda et al. 2007, comparing human maternal plasma, cord plasma and breast milk).

Milk and maternal blood can be used for biomonitoring and monitoring of POPs on an equal basis and are considered core media under the GMP. With regard to the intracompartmental comparability, both these media can be used to demonstrate possible temporal trends and regional variations in levels, and thus show effectiveness of regulations of the use of POPs.

One common criterion for selecting the donors among the two types of sampling studies (human milk and human maternal blood) is that samples should be collected from first-time mothers to obtain the complete picture of mothers' cumulative lifetime exposure and complete body burden (as POPs concentration decline over the course of lactation resulting in reduced body burden in mothers at subsequent births).

The following should be considered when choosing the sampling matrix:

- Human milk sampling is non-invasive and milk can generally be obtained from lactating mothers in reasonable quantities. In certain populations it may however be difficult to obtain human milk samples;
- Blood sampling is invasive and sampling of mothers prior to giving birth may readily be achieved. However, blood sampling may not be acceptable in certain cultures;
- Biological samples of human origin, like blood and milk, should always be considered a potential biohazard. Necessary precaution procedures should be applied to both sampling and handling of all samples, not only in situations where one may expect a problem, e.g. HIV-positive serology and hepatitis;
- The limit of detection for POPs will in general be lower in milk than in blood. The reason for this is partly the difference in lipids between the media and the fact that larger volumes of milk as compared to blood can normally be obtained;
- For less lipophilic substances such as PFOS the limit of detection will be considerably lower in blood than in milk as only a small (1%) and variable percentage is found in milk. When the limit of detection is approached the analytical precision will decrease.

4.2.3 Sampling and sample preparation methodology

The Global Monitoring Plan is using human milk and human maternal blood as the two equal core matrices for comparable biological monitoring. The 2007 edition of the WHO protocol and 2017 UNEP protocol lists the criteria for selection of mothers, and these should be followed as closely as possible. The most important criterion to be applied consistently in the selection of donors for both human milk and human maternal blood sampling is that donors should be first time mothers.

Number of samples/sampling location

The WHO guidelines (WHO, 2007) and amended UNEP guidelines (UNEP, 2017a) require samples from 50 individuals. However, current experience shows that some countries may not be able to recruit that many, and the proscribed collection period may therefore need to be extended to be able to collect 50 samples. Samples may also be collected from post-natal clinics.

The protocol also makes provision for a country to stratify the participants such that it represents the presumed exposure profile of each country. Elements that need to be considered here typically include

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

Questionnaire and informed consent

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

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

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

Sample handling

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

Human milk

Each of the 50 donors will contribute 50 ml of milk, of which 25ml is used for the pooled and back-up sample for additional analysis, as may be required,25 ml for individual analysis of basic POPs (if this is performed). d. During sampling of human milk from one mother the sample may be stored at 4 °C for a maximum of 72 hours. In countries where temperature control is not possible, the collection of milk samples should be done in bottles to which a tablet of potassium dichromate has been added (UNEP, 2017a). This method of preservation of the milk sample was applied successfully by some countries at the third round of WHO-coordinated exposure studies (van Leeuwen and Malisch, 2002; Schecter et al., 2003). For preparation of the pooled samples and transporting to the reference laboratory, see the UNEP guidance document.

Human blood

Sample handling is particularly important for obtaining homogeneous samples of human blood (plasma or serum) for analyses and to ensure sample integrity. Therefore, guidelines on handling of samples should be strictly followed (see Annex 4). Qualified personnel must be available to undertake the sampling and training may be required.

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

When pooling is required, 5 ml of each plasma sample is added, for a total of 250ml. Pooled samples can be stored at -70 °C until analysis. It can then be thawed to room temperature, be mixed by gentle inversion and the entire sample extracted. The container should be rinsed with solvents. Procedures for sample

handling during storage, transport to analytical laboratory and handling by analyst etc. should take into account the prevention of both cross-contamination by chemicals and infections.

Lipid adjustment of human blood and milk contaminant data

Since there are many factors that may affect the composition of human milk (Harris *et al*., 2001; Lovelady *et al*., 2002), note should be taken of the guidance in the Fourth WHO-Coordinated Survey (WHO, 2007).

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

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

Ethics

Each country will have to ensure that their protocols be approved by the relevant, ethical committees. Evidence of such approval should accompany the information package. In the case of human milk, the national protocol developed by each participating country is based on the WHO protocol (Malish & Moy, 2006; WHO, 2007). Any variation from the protocol, based on local ethical considerations, should be noted, and this should be included in the information package that accompanies the samples.

It should be noted that obtaining the ethical clearance of the national protocol is a lengthy process and participating countries should be aware of possible extended timelines in respect of this process in their planning work. It is important that the ethical clearance is actively facilitated to ensure timely implementation of the sampling activities.

HIV/AIDS

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

Transporting of samples

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

Interlaboratory comparison and cooperation issues

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

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

Furthermore, UNEP performs "Bi-ennial Global Interlaboratory Assessment on Persistent Organic Pollutants" (last available report: UNEP, 2017b), covering also human milk.

4.2.4 Special considerations for fluorinated POPs

Fluorinated POPs such as perfluorooctane sulfonic acid (PFOS) and its salts and perfluorooctanoic acid (PFOA) and its salts do not follow the "classical" pattern of partitioning into fatty tissues, but instead bind

preferentially to proteins in the plasma, such as albumin and gamma-lipoproteins, and in the liver, such as liver fatty acid binding protein (ref). This makes blood and liver the prioritised medium for PFOS and PFOA. The general analytical issues when determining PFOS is discussed in the analytical section (see Chapter 5).

In contrast to the other POPs analysis of the 'new' fluorinated POPs including PFOS and PFOA has only taken place since the beginning of 2000 when the first publications of PFOS in humans and the environment were published (Hansen et al., 2001, Giesy and Kannan 2001). The problems with the analysis and comparability of data were large and highlighted at a workshop in Hamburg and a subsequent paper (Martin et al. 2004). However, strong improvements in the analysis methods have been seen in subsequent years (e.g. Kärrman et al. 2007, 2009).

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

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

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

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

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

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

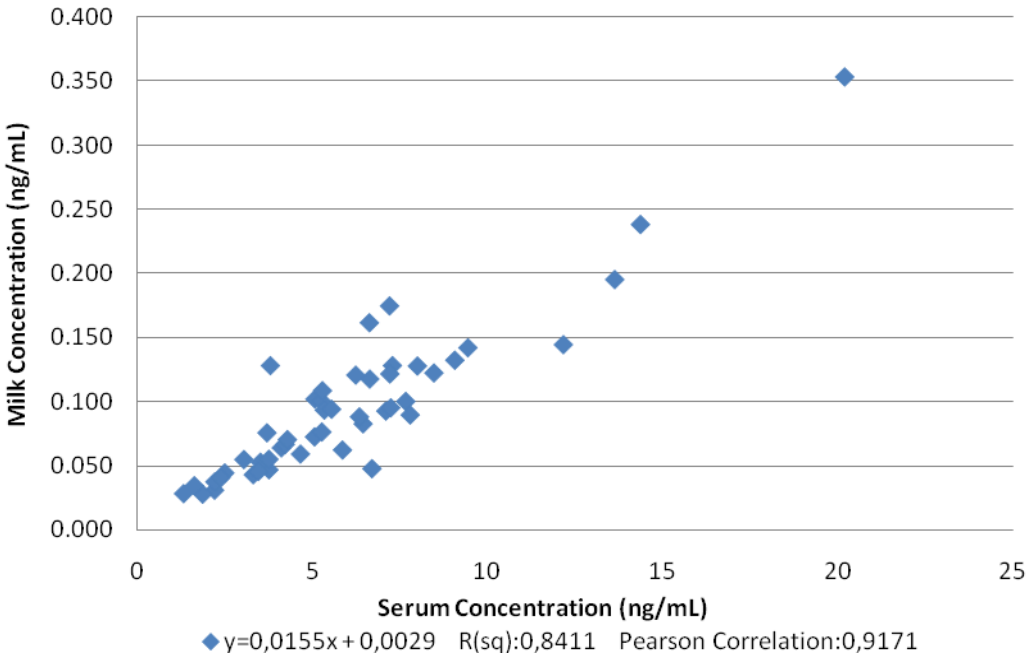


Figure 4.2.4: PFOS concentrations (ng/mL) in serum and milk samples from Sweden, 2004-2011. The linear equation of the line, including R^2, is given together with Pearson's correlation coefficient.

4.3 Water

4.3.1 Experimental design

Water has been identified as a core matrix under the GMP only for fluorinated POPs, based on the evidence that water is the main transport medium for these chemicals in the environment, the proven ability of numerous investigators to determine it in water and the availability of standard methods. PFOS is characterized by a relatively high water solubility, despite the hydrophobic tail, and water solubility is determined to 570 mg/L for PFOS (OECD 2002). PFOS (anion) is recommended for monitoring in water as a core matrix. Open oceans water column has been suggested to be a final sink of perfluorinated substances, such as PFOS and PFOA (Lohmann et al. 2013). Given the challenges of determining PFOS anion in air (see section 4.1.1) water represents the best environmental matrix for monitoring PFOS. A similar approach is valid for PFOA. A guidance for including PFOS to the GMP, complementary to this chapter has been published by the Chemicals Branch of the UNEP (Weiss et al., 2015).

Further fluorinated chemicals that are proposed for listing under the Convention, such as perfluorohexane sulfonic acid (PFHxS) are suitable for monitoring in water under the GMP based on the availability of methods to determine them in water samples collected for PFOS / PFOA analysis.

Sampling locations

The Second Global Monitoring report (UNEP/POPS/COP.8/INF/38) reported results for PFOS for approximately 450 freshwater or estuarine locations globally based on a review of the peer reviewed literature and results from national programs for the period 2004 to 2014. The majority of the data were from the northern hemisphere: WEOG and Asia-Pacific regions. The major lesson learned from this assessment was that national programs had very limited data with the majority coming from individual studies published in peer reviewed journals by university and government researchers. Thus to assess temporal trends related to the effectiveness of global phase outs under the Convention, the next global assessment of PFOS in water and will have to utilize that information as a baseline. This will require careful assessment of the individual studies and sampling sites to confirm that they meet the criteria for site selection and analysis.

Results for rivers offer perhaps the best opportunity to assess temporal trends due to reductions in emissions provided that sources e.g. WWTPs, tributaries, accidental spills etc, are well documented. For oceans, monitoring results along key cruise transects sites as discussed in Section 4.3.4.1 will be critical information. Recommendations for selection of sampling locations are as follows (Weiss et al., 2015):

- Define the objectives of the project and the selected monitoring site;
- Gather hydrological and other relevant data (presence of industry and WWTP, population density, etc.);
- For monitoring purpose estuaries are recommended as sampling sites, but data from other sites are welcome and should have one of the following characteristics:
    - Estuary (see for US EPA for guidance on both small, discrete site (<10 km2) and larger tidal rivers and bays [49]);
    - River downstream populated area (sufficient mixture distance from any influent);
    - Lake with a defined surrounding population;
    - Tributary (before entering the main stream);
- Adapt the distance to shore to existing circumstances at the site. Make sure the water sampled is from a zone where it is mixed;
- Ease of access by limnological or oceanographic vessels with capacity to deploy water sampling equipment or from land based sites such as bridges.

Siting considerations

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

Requirements for water sampling sites include:

- Ease of access by limnological or oceanographic vessels with capacity to deploy water sampling equipment or from land based sites such as bridges;
- Presence of an existing routine sampling program with water chemistry data;
- Availability physical measurements (temperature, pH, conductivity), flow;
- Meteorological observations;
- Personnel who could be trained in the sampling techniques;
- Availability of suitable laboratory facilities to prepare sampling media and subsequently extract and analyse the samples.

Sampling frequency

The sampling frequency has to be realistic in terms of number of samples (costs and logistics), but still represent a statistical validated set of samples for the monitoring purpose. Both the temporal and spatial sampling design need to have sufficient resolution. Grab samples of surface water samples could be used to see temporal and regional variations and the sampling frequency should be high enough to filter out short term variability (e.g., precipitation events).

Recommended minimum and optimum frequencies are listed according to the “Water Quality Monitoring - A Practical Guide to the Design and Implementation of Freshwater Quality Studies and Monitoring Programmes” (UNEP/WHO, 1996) and sampling frequencies for PFOS has been recommended in the guidance on PFAS analysis in water for the GMP on POPs (Weiss et al., 2015). For the frequency of the sampling of PFOS in water it is recommended to:

- Sample at a selected site 4 times a year (same site and with the same method);

- Carefully determine the sampling occasions depending on optimal conditions, preferably consistent between years (e.g., 2 times high- and 2 low-water stage, although avoiding drought conditions or freezing conditions.

4.3.2 Sampled matrix

Surface freshwater or seawater phase should be sampled for the monitoring of PFOS in water under GMP. Determination of POPs in ground waters or in drinking water is not envisioned. Aquatic biota (e.g., fish, invertebrates), reflects the POPs level in the surrounding water, sediment, and food web. POPs data for biota are discussed under 4.4. “Other media”.

4.3.3 Sampling and sample handling

Collection of seawater samples has been done through ship intake systems (Ahrens et al. 2009a) and via Niskin bottles (Yamashita et al. 2004) into plastic or glass bottles. In lakes and large rivers, direct pumping into sampling bottles (Furdui et al. 2008) and collection from Niskin type samplers (Scott et al. 2009; Scott et al. 2010) and from ship intakes (Ahrens et al. 2009b) has been used. Samples for PFOS analysis have generally not been filtered prior to extraction. A recent study of waters in the Elbe River (Germany) and the North Sea indicated that on average 14% of PFOS was in the particulate phase (Ahrens et al. 2009b). In ocean waters PFOS was not detectable on particulates (Ahrens et al. 2009a) likely because of the lower SPM and thus filtration is not recommended, unless it can be done with an inline system or in a clean room (Ahrens et al. 2009b) because it could introduce contamination. Contamination is also introduced from polytetrafluoroethylene (PTFE) materials due to the use of perfluoroctanoate (PFOA) as a processing aid for PTFE production. Common sources are PTFE tubing, o-rings and other seals. PTFE bottles or bottles with fluorinated interior coatings and these should be avoided.

Details of recommended sampling procedures under the GMP can be found in a guidance for monitoring PFASs in water for the GMP (Weiss et al., 2015):

- Active/grab sampling is the recommended method;
- Use, e.g., NIskin™ or other remotely activated water samplers, or simply hand-dipping;
- Avoid sampling the surface;
- For sampling use a 500 mL wide mouth HDPE bottle;
- Use HDPE sampling and storage containers (sampling bottles, test tubes, vials etc.);
- All material should be rinsed with methanol before usage;
- Analysis volume is typically 50 mL-500 mL and should be determined by the analytical laboratory;
- To avoid cross contamination the sample bottles should only be used once;
- Take two samples, one for analysis and one for later confirmation if needed;
- Store the samples in the fridge until analysis;
- It is recommended to perform a pilot sampling to establish the levels and practice the sampling.

For PFOS and other PFASs it is recommended that containers (sampling bottles, test tubes, vials etc) should be of high density polyethylene (HDPE) material to avoid sorption to the material l (Berger et al. 2011; Ullah et al. 2012). If the goal is to include analyses of other PFAS compounds, PTFE material should be avoided (e.g., it is often used to line the interior of samplers such as Niskin™, GoFlo™ bottles and tubing, as that is a source of PFOA and PFNA(Yamashita et al. 2004). To minimize contamination sources use the strategy of clean-hands/dirty hands while sampling, i.e. be two persons taking the sample, one is holding the sample equipment (clean-hands) and one person do the sampling (dirty hands). Sample caps should also be checked to confirm that they have HDPE liners.

Sampling volume is determined by the analytical laboratory and should be adapted to expected PFOS levels and analytical capacities. The instrumental limit of detection is the main factor limiting the sensitivity and the volume should be enough to reach quantification levels.

Sampling volume for PFOS and other PFASs is typically 100-500 mL. It should be determined by the analytical laboratory and adapted to expected PFOS levels and analytical capacities. The instrumental limit of detection is the main factor limiting the sensitivity and the volume should be enough to reach quantification levels.

Sampling should be done below the surface to avoid possible surface film contamination. NIskin™ or other water samplers which area activated by dropping a "messenger" to close the sampler at a prescribed depth are idea for lakes and larger rivers/estuaries. Hand sampling in which HDPE bottles are uncapped under the surface (~0.5 m) is adequate for shallower water bodies. Wide mouth bottles are best for rapid filling of the container. A small headspace should be left before capping to avoid bottle breakage if samples are frozen.

Recently, a novel device for the onsite large-volume SPE (LVSPE) was developed (Schulze et al., 2017). It is an automated device for the unattended and representative sampling according to international standards (e.g. (ISO, 2006)) and combines of SPE with a pre-filtration cartridge to separate suspended particulate matter (SPM) from the water phase.

Measurement of PFOS in water indirectly by deploying passive samplers remains an option for future (Lohmann 2017). To date no passive sampler suitable for routine monitoring of PFOS under GMP is available, although some promising research results have been published recently (Kaserzon et al., 2012, 2013, 2014, 2019). In spite of these shortcomings, passive samplers of PFASs could in future be an alternative method in situations where the classical monitoring approaches have insufficient low limits of detection or low frequency spot sampling fails.

4.3.4 QA/QC and Data Treatment

Quality control procedures are required for the collection of environmental water samples for the following reasons to:

- Monitor the effectiveness of sampling methodology;
- Demonstrate that the various stages of the sample collection process are adequately controlled and suited to the intended purpose, including adequate control over sources of error such as sample contamination, loss of analyte, and sample instability. To achieve this quality control, procedures should provide a means of detecting sampling error and hence a means of rejecting invalid or misleading data resulting from the sampling process;
- Quantify and control the sources of error which arise in sampling. Quantification gives a guide to the significance that sampling plays in the overall accuracy of data.

A series of guidances dealing with sampling in surface waters and marine waters has been published by ISO and those general rules should be followed to assure quality of the sampling process (ISO 1992, ISO 2014a, ISO 2016) Guidance on the selection and use of various quality assurance techniques relating to the environmental water sampling is provided by an ISO norm (ISO, 2014b).

As discussed for air sampling media, special attention needs to be paid to potential sample contamination during sample preparation, sampling, transport, storage and laboratory processing. Sorbents materials applied in solid phase extraction are typically pre-cleaned by sequential Soxhlet extraction using a combination of polar and non-polar solvents. Pre-packaged media such solid phase cartridges are conditioned by elution with a polar and non-polar solvent combination in the analytical laboratory or (if conditions permit) in the field prior to use. Glass fiber filters must also be baked (350 ^{o}C) prior to use and stored in a sealed container.

Additional precautions for solid phase sampling systems are (1) field blanks consisting of the same media that are exposed to the ambient air during sample handling in the field (2) laboratory blanks of sorbent materials prepared at the same time as the field blanks and held in the laboratory. Comparison of the field and laboratory blanks permits and assessment of contamination during sampling and sample transport.

Purified laboratory water, e.g., MilliQ™ or distilled water can be used but should be confirmed to be free of PFASs. Typically lab purified waters are not good blanks due to presence of low level PFAS contamination (Weiss et al., 2015).

Containers (sampling bottles, test tubes, vials, *etc.*) should be of high density polyethylene (HDPE) material to avoid sorption of PFOS to the material (Berger et al., 2011; Ullah et al., 2012).

There are recently no certified reference materials available for PFOS in surface water. Very recently, JRC-IRMM released a reference material certified for PFOS and other perfluoroalkyl substances in drinking water (https://ec.europa.eu/jrc/institutes/irmm/; IRMM-428; certified value 9.6±1.7 ng L^{-1}). This CRM is, to the best of knowledge, the only RM on the market certified for PFOS. Regrettably, it cannot be considered fully representative of a surface water sample which include suspended particulate matter and/or more or less dissolved organic matter (Ricci et al, 2016).

The routine laboratory performance studies provide the basis of external quality assurance for institutes that make regular chemical measurements in the aquatic environment. A proficiency testing (PT) provider WEPAL-QUASIMEME (www.quasimeme.org) organises laboratory performance studies in support of marine environmental monitoring and has previously included laboratories in North America and Asia-Pacific. Although they provide test materials for analysis of perfluorinated substances, the analysed matrices currently include sediment and biota, but no surface water. Also Canada's Northern Contaminants Program and the Arctic Monitoring and Assesssment Program have conducted interlaboratory studies on PFASs annually for the past 10 years. Currently, some PT providers offer testing of PFOS analysis in surface water (https://aqs.iswa.uni-stuttgart.de/rv/index.html).

4.4 Other media

4.4.1 Introduction

The 2016 GMP global monitoring report (UNEP/POPS/COP.8/21/Add.1) states:

> In 2007, the SC COP3 decided that for the GMP under Article 16 the core media would be air and human tissue (milk, blood); the reasoning behind this choice still stands. The importance of other media beyond core media to understand and assess changes over space and time of the risk posed by POPs to humans and the environment is indisputable. The choice of core media is based on strategic long term priorities in the context of a global exercise with very limited resources. Measurements in air and humans provide very valuable information that is globally comparable over space and time, if and only if, measurements are shown to follow agreed QA/QC procedures. Good quality measurements in other media are central and indispensable to gauge the importance over time of biogeochemical and commercial pathways of POPs mixtures in the local environment and the consequent exposure routes to humans and ecosystems.
>
> There is no systematic compilation of guidance for the sampling and analysis of POPs in other media under the GMP.
>
> ***Recommendation****: Refer to guidance and QA/QC documentations from established monitoring programmes, e.g. AMAP/NCP, the Helsinki Commission (HELCOM), the Commission for the Protection of the Marine Environment of the North-East Atlantic (OSPAR), in order to obtain comparable data.*

This chapter intends to identify technical guidance provided by long term monitoring programs of POPs such as UNEP, Arctic Monitoring and Assessment Programme (AMAP)/Northern Contaminants Program (NCP), Integrated Atmospheric Deposition Network (IADN), Monitoring and Surveillance in the Great Lakes Basin (GLB), Convention on Long-Range Transboundary Air Pollution (CLRTAP)/ The European Monitoring and Evaluation Programme (EMEP), the HELCOM, OSPAR, Japan, Monitoring and management of POPs in Asia (UNU-IAS) and the EU Water Framework Directive (WFD).

The list of substances and analytes of interest are described in detail in Chapter 2 of this document. For the purpose of this chapter 31 large groups are considered:

1. Aldrin
2. Alpha-hexachlorocyclohexane (α-HCH)
3. Beta-hexachlorocyclohexane (β-HCH)
4. Chlordane
5. Chlordecone
6. Dichlorodiphenyltrichloroethane (DDT)
7. Dieldrin
8. Endosulfan
9. Endrin
10. Gamma-hexachlorocyclohexane (γ-HCH)

11. Heptachlor
12. Hexabromobiphenyl (HBB)
13. Hexabromocyclododecane (HBCD)
14. Hexabromodiphenyl ether and heptabromodiphenyl ether (PBDE)
15. Hexachlorobenzene (HCB)
16. Mirex
17. Pentachlorobenzene (PeCBz)
18. Perfluorooctane sulfonic acid (PFOS)
19. Polychlorinated biphenyls (PCB)
20. Polychlorinated dibenzo-para-dioxins (PCDD)
21. Polychlorinated dibenzofurans (PCDF)
22. Tetrabromodiphenyl ether and pentabromodiphenyl ether (PBDE)
23. Toxaphene
24. Hexachlorobutadiene (HCBD);
25. Pentachlorophenol (PCP);
26. Polychlorinated naphthalenes (PCNs);
27. Decabromodiphenyl ether (decaBDE; BDE-209);
28. Short-chain chlorinated paraffins (SCCPs).
29. Dicofol;
30. Pentadecafluorooctanoic acid (PFOA), its salts and PFOA-related compounds;
31. Perfluorohexane sulfonic acid (PFHxS), its salts and PFHxS-related compounds.

A number of well-established long term monitoring programs have been indispensable strategic partners of the SC GMP effort, this chapter is based on documents produced by these main sources UNEP, OSPAR, HELCOM, EMEP, AMAP/NCP, monitoring and surveillance programs in the Great Lakes region, Japan and the EU WFD.

In particular, for POPs other than PFOS listed under SC - water is considered as “other matrix”. HCH isomers can also be determined relatively easily in water. Since substantial data exists for them in air and another matrix is not absolutely essential for evaluating effectiveness of the Convention. However, since the data is available, it may be beneficial to utilize them for assessment.

Determination of very hydrophobic POPs in water (approximately with log Kow>6) is generally challenging in discrete water samples, due their very low concentrations (typically in pg/l range) which are often close to method detection limits. In addition, measurement of concentrations close to detection limits is associated with increased quality control issues such as contamination during sampling, transport and sample processing in the laboratory. Nevertheless, most of the neutral hydrophobic POPs can be easily analysed in water after in situ concentration by passive sampling techniques. So far, most of them are being monitored in air or human breast milk and monitoring in water matrix has not been considered essential for evaluating effectiveness of the Convention. From the five new POPs listed in the Convention in 2015 and 2017, substantial data on pentachlorophenol in water exists from various pesticide monitoring programmes, but for GMP monitoring of pentachloroanisole (PCA) in ambient air is recommended for reporting.

Table 4.4.1: Substances monitored by the different programs in air, water, sediments and biota.

		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
AMAP/NCP	Air																															
	Water																															
	Biota																															
LRTAP/EMEP	Air																															
	Dep.																															
G Lakes N.A	Air																															
	Water																															
	Sediment																															
	Biota																															
OSPAR	Water																															
	Sediment																															
	Biota																															
HELCOM	Water																															
	Sediment																															
	Biota																															
Japan	Air																															
	Water																															
	Sediment																															
	Biota																															
Asia (UNU-IAS)	Air																															
	Water																															
	Sediment																															
	Biota																															
EU WFD	Water																															
	Sediment																															
	Biota																															

In 2007 UNEP elaborated a guidance document (UNEP, 2007) that describes in detail sampling design, sample preparation and analysis, QA/QC in all media for legacy POPs. UNEP (2007), although nearly 15 years old, is still applicable and can be used as a starting point. Chapter 5 in the UNEP (2007) document covers most aspects of the analytical methods for other media.

AMAP has produced an outstanding corpus of knowledge in methods, documents and data on POPs. In this chapter, we refer to some recent documents where POPs measurements are reported and interpreted in an ecosystem and public health integrated approach. (AMAP 2015, 2016, 2017).

EMEP (EMEP 2001) keeps an updated SOP manual to sample POPs in aerosol, wet/ dry deposition.

Multiple programs have been involved in monitoring of hazardous substances Great Lakes of North America over four decades in the framework of a binational agreement. (EC and USEPA 2014).

OSPAR (OSPAR 2013) has produced over many years solid guidance on sampling design, sample preparation and analysis for POPs in marine water, sediment, and biota. The OSPAR guidance is a useful start and could be used as the default methods. They apply to marine biota but many aspects also apply to freshwater biota. There are also OSPAR guidelines for sediments (2013).

HELCOM relies to a large extent in OSPAR for the SOP and covers also terrestrial and freshwater monitoring.

In Japan, the Ministry of the Environment has measured POPs in wildlife from 1978, in sediments from 1985, and publishes environmental monitoring results of POPs, dioxins/furans/dl-PCBs (dioxins/furans and dl-PCBs are monitored separately from other POPs because these unintentionally released POPs are regulated under a different law) and dioxins and some of POPs in marine environment every year. The latest publications can be found in JMOE (2016 POPs, 2017 Dioxins, 2017 Marine). The description of the samples are included in these documents and also in NOWPAP POMRAC (2015): air, surface water, sediments and biota (fishes, bivalves, birds and eggs) are analyzed for POPs while air, surface water, ground water, soils and sediments are analyzed for dioxins/furans/dl-PCBs.

Information on the current POPs monitoring in other media of East Asian countries can be found in UNU-IAS (2015) and NOWPAP POMRAC (2015).

The Water Framework Directive 2000/60/EC (WFD), has published a Guidance for sediment and biota monitoring under the Common Implementation Strategy for the Water Framework Directive (Carere et al 2012).

It seems to be the case that, based on general guidance, in the end each national program dictates field sampling methods to be used because the work on POPs has to be compatible with existing programs and infrastructure, and consequently comparability of data depends on methods inter-calibration and participation in QA/QC exercises.

4.4.2 QA/QC and Data Treatment

There will be other sections in this document dealing with this issue, one key message should be that comparing data generated inside programs (or as reported by programs) is feasible but comparing across programs can be difficult and misleading.

4.4.3 Considerations for time trend analysis

The AMAP 2015 report on temporal trends in POPs in the Arctic provides a very informative summary of available data on POPs concentrations in the environment in recent decades and describes useful methods to study changes of the chemical landscape over time.

4.4.4 Specimen banking

Specimen banking is obviously central for work on other media and has shown its value.

The GMP 2016 global report states that:

> Natural archives (e.g. sediment and ice cores, tree rings, etc.) and sample banks have shown to be useful for retrospective analysis for the occurrence and changes over time of POPs, in particular for newly listed substances, as well as to increase spatial coverage in regions with limited data.
>
> ***Recommendation:*** *Encourage information exchange through collaboration with existing monitoring programmes and sample banks in other media to support GMP data need.*

We refer to chapter 8 of this document “Many of Environmental Specimen Bank facilities have made Standard Operational Procedure (SOPs) for the sampling and / or storage procedures, and some are made available through websites or other means. The International Society of Biological and Environmental Repositories (ISBER) provides an international forum that addresses the technical, legal, managerial, and ethical issues relevant to repositories associated with biological and environmental specimens. Through member contributions, ISBER has developed and published the 4th edition of “ISBER Best Practices: Recommendations for Repositories” (Campbell, et al., 2018).

Fliedner et al (2016) shows how specimen collections can be very effective in the context of the WFD, the SC GMP and a wider understanding of changes in the chemistry of the environment.

4.4.5 Data flow, models and archive

Multimedia ecosystem modeling of POPs is central to interpret long term monitoring data and establish links with actions undertaken. There are many important questions to be studied concerning pathways and time-lags between releases, control measures and levels in the environment and humans. Thus making good use of the rich collections of POPs monitoring data over four decades in the context of ecosystem and LRT models will be central to design effective actions, prevent predictable mistakes and will also enhance scientific understanding of ecosystem dynamics. An illustration of such integrated work can be found in (AMAP 2016).

5 ANALYTICAL METHODOLOGY

5.1 Sampling

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

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

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

5.2 Extraction and clean-up

The appropriately prepared sample can be extracted by a variety of techniques. The main points to consider are to use an appropriate solvent or solvent mixture (depending on matrix, kind of preparation of the matrix such as drying or not before extraction and depending on the kind of analyte), to allow adequate time of exposure of the solvent system in the sample matrix. Extraction techniques can be based on Soxhlet, Twisselmann hot extraction, or semi-automated systems (pressurized fluid extractors/pressurized liquid extractors, *e.g.*, as described in EPA method 3545A for soils or sediments). Extractions can also be accelerated by the use of ultrasonication. Cross contamination from residues left behind by high levels of POPs in other samples is a concern at this stage and equipment must be thoroughly cleaned and checked from batch to batch. Internal standards should be added before extraction allowing to control the efficiency of the extraction and clean up procedure.

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

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

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

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

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

Analytical methodology for PCDD/PCDF and dioxin-like PCB differs from that used for routine indicator-PCB and OCPs in that it requires much lower detection limits (typically 10-100 times lower) because they occur at very low concentrations and guideline limits in food or feedingstuffs are in the low pg/g or ng/kg or range per sample; the Provisional Tolerable Monthly Intake is 70 pg/kg body weight (Joint FAO/WHO Expert Committee on Food Additives (JEFCA), 2001). To enforce and control these low concentrations for PCDD/PCDF isotope dilution MS (use of 13C-surrogates for all PCDD/PCDF homologue groups), enrichment on carbon to isolate planar compounds, very small final volumes (10 μL-50 μL) for GC-HRMS quantification is used. Methodology for PCDD/PCDF, slightly modified to include the dioxin-like PCB, developed by the US EPA (method 1613) or based on the European Standard (EN 16215), is well established and validated by numerous inter-laboratory comparisons. Differences between the calibration ranges of the US EPA method 1613 and the EN 16215 method in particular with regard to the highest calibration point and possible toxicological concern are discussed as part of an assessment of analytical work in a dioxin laboratory (Malisch et al, 2017). Such methodology would be recommended for use in a global monitoring programme. Such guidance for the extraction, isolation and quantification of PCDD/PCDF is recommended in order to be in compliance with ongoing programmes and compatible with results generated with these methods over the past ten years.

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

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

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

Guidance for extraction of PFOS and related PFCs from water has been provided in Section 4.2.2 and Ahrens et al. (2010) For water an ISO method has been developed (ISO 2008) in which PFOS and other PFCs are extracted from water with weak anion exchange (WAX) solid phase cartridges. However, this method has a limit of quantification of 10 ng _L-1 only, whereas for environmental samples such as sea water typically contains concentrations at pg L-1 levels. As described for blood serum, the PFCs are then eluted from the cartridges in two fractions. The first fraction is methanol and contains PFOSA and other neutral PFCs, whereas the second fraction is obtained with 4 mL of 0.1 % ammonium hydroxide in methanol and contains the PFOS. In general no further cleanup of extracts for PFOS is required and samples can be submitted for LC-tandem MS analysis as discussed below. Where cleanup of water extracts is required due to co-extractive materials interfering with chromatography or suppressing ionization in the mass spectrometer, Ahrens et al. (2010) recommend the use of a carbon column cleanup

with ENV CARB cartridges. The PFCs are generally not absorbed by the carbon whereas lipophilic and pigmented co-extractives are usually retained.

A critical feature of all methods for PFCs that employ LC-MS/MS is the use of 13C- and/or 18O2-labelled PFOS and PFOSA substances from the extraction step. The isotope-dilution technique, which uses isotope-labeled internal standards chemically identical to the analytes of interest, corrects for the matrix effects on the analytes recovery during the extraction procedure and in their extent of ionization, thus resulting in greater accuracy and precision.

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

5.3 POPs analysis

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

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

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

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

GC-ECD – gas chromatography/electron capture detection
GC-LRMS – gas chromatography/low resolution mass spectrometry
GC-HRMS – gas chromatography/high resolution mass spectrometry
LC-MS/MS – high performance liquid chromatography/tandem mass spectrometry

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

		USD
Instrumentation - Analytical laboratory		
GC-ECD with autosampler	Investment	40,000
GC-LRMS with autosampler	Investment	140,000
GC-HRMS with autosampler	Investment	700,000
LC-MS/MS with autosampler	Investment	200,000
Air samplers		USD
Low-volume sampler	*per* piece	10,000
Passive air sampler	*per* piece	150
Grab water sampling bottle with cap (500 mL)	*per* piece	5
Consumables		
Quartz filter plus PUF plugs	*per* set	
Pre-cleaned PUF plugs/disks	*per* disk	20
Analysis to third parties (cost per sample)	Preferred method	USD
PCDD/PCDF	HRGC-HRMS	900
dl-PCB (when in addition to PCDD/Fs)	HRGC-HRMS	350
PCNs	HRGC-HRMS	450
TEQ (total)	HRGC-HRMS	1,150
POPs pesticides+indicator PCB+ endosulfan (without toxaphene)	HRGC-HRMS, HRGC-LRMS, HRGC-ECD	700
Toxaphene	HRGC-LRMS, HRGC-HRMS	350
PBDE+PBB153+HBCD screen	HRGC-LRMS, HRGC-HRMS	450
HBCD isomers (LC)	LC-MS/MS	350
PFOS (air, blood)	LC-MS/MS	350
PFOS (water)		250
Materials and consumables		USD
HRGC columns (60 m)	*per* piece	880
Native pesticides standard mix	*per* unit	200
Labelled LRMS pesticides standard mix (calibration, clean-up, syringe)	*per* set	5,200
Labelled indicator PCB standard mix (calibration, clean-up, syringe)	*per* set	1,500
Labelled LRMS PCDD/PCDF standard mix (EPA 8280, calibration, clean-up, syringe)	*per* set	4,200
Labelled HRMS PCDD/PCDF standard mix (EPA 1613, calibration, clean-up, syringe)	*per* set	2,820

		USD
Labelled HRMS dl-PCB standard mix (WHO-TEF mix, calibration, clean-up, syringe)	*per* set	2,100
Labelled MS PBDE standard mix (calibration, clean-up, syringe)	*per* set	
Labelled MS PFOS standard mix (calibration, clean-up, syringe)	*per* set	

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

During the period of the first phase of Global Monitoring Plan leading to the first regional and global reports, recommended methods and instrumentation as shown above have been applied and shown useful. During 2013/2014, the analytical methods for the analysis of the new POPs have been developed and successfully pilot-tested in four developing countries. The new POPs have also been included into the second round of the Bi-ennial interlaboratory assessment for POPs laboratories. Further, improved methods as they may appear over the life of the Global Monitoring Plan can be included into the guidance document and adopted.

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

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

Numerous analytical approaches are available for quantifying PCB, and OCPs, as well as PCDD/PCDF by gas chromatography. As with extraction/separation steps only general guidance is required for ortho-substituted PCB and OCPs. Some general guidance on the application of gas chromatographic analysis of ortho-substituted PCB and OCPs is provided in Table 5.2. For PCDD/PCDF and dioxin-like PCB, quantification solely by isotope dilution HRMS is recommended and details can be found in standard operation procedures (SOPs) (e.g., EPA method 8290A, EPA methods 1613 and 1668, EN 16215).

Obviously, HRMS can also be used for the determination of all PCB, including congener-specific determination of non-ortho and mono-ortho substituted PCB (e.g., EPA method 1668 and EN 16215) as well as OCPs and indeed would provide a very high level of confidence in the results compared to GC-ECD. However, use of GC-ECD is recommended for indicator PCBs because of its wide availability, relatively low cost, and the substantial knowledge base that exists on the use of this technology for analysis of di-ortho PCB at low ng/g levels or higher in environmental matrices. Due to the inherent high transformation of PBDE in the environment, especially light-induced, it is not recommended to use a combination of GC columns and ECD detection for the eight indicator PBDE. OCPs are often analysed by GC-ECD but the analysis can be performed with much better accuracy by GC/MS and use of labeled standards. Another recent development are Time-of-Flight MS instruments (ToF-MS). These bench-top MS instruments nowadays offer resolution that even exceeds the traditional HRMS instruments. It is expected that in the near future these instruments will replace the traditional HRMS sector instruments, also for the analysis of PCCD/Fs and non-ortho PCB.

Isotope dilution high resolution gas chromatography and high resolution mass spectrometry (HRGC/HRMS) methods is recommended for PCNs analysis. Peaks corresponding to the individual PCN congeners can be identified based on their retention times relative to those of internal standards and by their ion ratios.

SCCPs include a large number of isomers, and their analysis is very challenging. Among various methods developed to date (van Mourik et al. 2015, Yuan et al. 2019), congener-group specific quantitation

methods seem to be promising and beneficial due to their inherent comparability and capability to trace sources. Currently standards of each congener-group or known congener-group composition are lacking, and the quantitation is conducted by estimating RF of each congener-group based on the analysis of a series of standard mixtures with fixed carbon length and different total chlorine contents (Takasuga et al. 2011, Yuan et al. 2017). An extremely high separation power of GCxGC combined with ECD or TOF-MS may have a potential to separate and quantitate each congener group from mixtures directly (Xia et al. 2014, 2016).

Similar and comparable composition of SCCP mixtures were reported among different analytical methods, i.e., (APCI-QTOF-MS, GC/ECNI-sector-MS, and GC/ECNI-QOrbitrap, Yuan et al. 2017), (GC/ECNI-TOF-MS, LC/APCI-TOF-MS and LC/ESI-TOF-MS, Hanari and Nakano, 2019), and (LC/ESI-MS/MS and GC/ECNI-Orbitrap, Matsukami et al. 2020) when using the same set of standards for congener-group specific quantification. These results strongly support the view that congener-group specific approach will give us comparable and reliable concentration of SCCPs, and stress the importance of establishment of standards of each congener group or with known congener-group compositions. SCCP produced as a candidate reference material (Hanari and Nakano, 2019) will be useful to support QA/QC, or as standards for quantitation.

SCCPs tend to be fragmented by EI, and ECNI is commonly used as an ion source for GC/MS. However, due to ECNI's inferior sensitivity against lower chlorinated SCCP, EI is also used frequently for the analysis of congeners with chlorine atoms equal or less than four. In ECNI, removal of chlorine or hydrogen chloride from SCCP congener during ionization process is common, and makes the mass spectrum even more complicated. Other organochlorines, such as PCB, also show similar mass and interfere the SCCP analysis. Interferences from other organochlorines can be eliminated by careful clean-up procedure and GC/high resolution MS, such as TOF-MS. Interferences from MCCPs and SCCPs, on the other hand, are difficult to eliminate by chromatography or clean-up process. Part of them can be eliminated by TOF-MS, but it is reported that an extremely high mass resolution above 50,000 is needed to eliminate all the known interferences and quantify SCCPs accurately (Krätschmer et al. 2018).

LC/MS methods depend on adduct formation for the ionization of SCCPs. For APCI ion source, several adduct formation methods have been reported, including chlorine, bromine (Yuan et al. 2019) and oxygen (Ministry of the Environment, Japan 2005). For ESI, acetate adduct is a choice (Matsukami et al. 2020). MCCP is the dominant source of interference for the SCCP analysis in LC/MS, and the interferences seem to be removed efficiently by using high resolution mass spectrometer, such as TOF-MS (Hanari and Nakano, 2019). Alternatively, use of cyanopropyl column was reported to separate MCCP interference from SCCP efficiently (Matsukami et al. 2020). By using this column, the authors showed quite comparable data between LC/ESI-MS/MS with acetate buffer and GC/ECNI-Orbitrap for a variety of CPs mixtures, including MCCP and SCCP mixtures).

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

For water samples, the following orientation could be helpful:

	Unit	HRMS	LRMS	ECD
PFOS and other anionic PFAS	pg L^{-1}		5-10	

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

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

Notes:

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

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

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

5.4 Data treatment

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

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

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

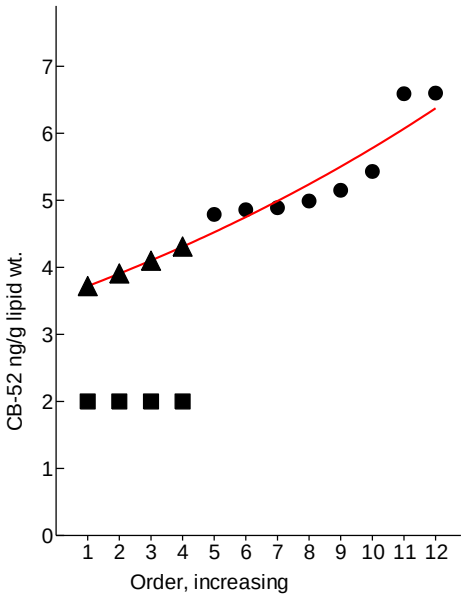


Figure 5.2: Example of substitution of concentrations reported as less than LOD, by extrapolation from regression of concentrations from the same annual sample above LOD on rank order. Log-linear regression fitted to data above LOD. Dots = concentrations above LOD, Triangles = substituted values for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

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

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

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

5.5 Organization of quality control

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

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

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

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

As orientation, the "Guidance document on analytical quality control and method validation procedures for pesticide residues and analysis in food and feed" gives a comprehensive overview on analytical quality control in the field of pesticide analysis (European Commission, SANTE/11813/2017). Furthermore, Commission Regulation (EU) 2017/644 sets analytical criteria for the control of levels of dioxins, dioxin-like PCBs and non-dioxin-like PCBs in certain foodstuffs, including performance characteristics as trueness, intermediate precision and the acceptable difference between upper and lower bound TEQ calculations (Commission Regulation (EU) 2017/644). In this regulation on dioxin analysis, also a link to a "Guidance Document on Measurement Uncertainty for Laboratories performing PCDD/F and PCB Analysis using Isotope Dilution Mass Spectrometry" and a "Guidance Document on the Estimation of LOD and LOQ for Measurements in the Field of Contaminants in Feed and Food" is made. In general, such guidance documents and criteria are a valuable orientation also for other matrices and contaminants.

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

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

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

6 DATA HANDLING

6.1 Objectives and priorities

Data handling under the Global Monitoring Plan is responsibility of the members of individual Regional Organization Groups (ROGs) and the Global Coordination Group (GCG) as specified in Chapter 1 of this guidance. The objective of the GMP is to determine changes in concentrations of listed POPs over time and identification of trends from monitoring of POPs globally to support the effectiveness evaluation of the Stockholm Convention as specified in Article 16 of the Convention.

GMP data generated and provided need to be comparable, validated and harmonized and capable of revealing trends over time in emissions and/or exposure to contaminants of concern, in the various regions. To this end, Global Monitoring Plan data warehouse (GMP DWH), an electronic tool containing a multilevel data repository, analytical tools and a visualization platform has been developed and is available to the ROGs for their work with POPs monitoring data since 2014.

A major focus of the work in the second phase of the GMP has been to provide support to the ROGs with enhanced harmonized data handling for the compilation, processing, storing and presentation of their data. A GMP data warehouse supports data handling and assists the regional organization groups and the global coordination group in producing the regional and global monitoring report. The database processes, design and functionalities have been discussed and agreed upon by the global coordination group. It includes an interactive on-line data capture system, handling, and a presentation module. The compiled information is available to the ROGs for the development of the monitoring reports and to other scientists to work with the data in statistical analysis and mathematical models.

The data evaluation procedure including their validation by the regional organization groups supports comparability of the different samples, especially from the point of view of the type of site, matrix, sampling method, time span and sampling frequency. The data warehouse also includes data visualization tools and means for statistical and trend analysis. Details on statistical considerations are available in Chapter 3.

6.2 Data policy

6.2.1 Terminology

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

- **Primary GMP data**: are the results of measurements of POPs concentrations in samples of core matrices collected for the GMP, or other programmes that are compatible with the goals of the GMP. They include both measurements of POPs in specific samples, and measurements of other covariables relating to these samples (*e.g*. biological covariates), that are necessary to interpret the POPs data in a meaningful way, including the location and timing of sampling;
- **GMP meta-data:** are any other data or information that describe the *primary GMP data* in some way. This can include information on the methodologies employed (*e.g*., for sampling and analysis) and the laboratories responsible for a particular set of analyses, or the design and implementation of programmes that contribute to the GMP, etc. Please note that summary information on programmes, chemicals monitored, data available and data structure is available in the GMP DWH and can be directly copied to a regional/global report;
- **Supplementary data:** Are any other data or information that may be accepted for use in the Stockholm Convention evaluation process. This might include relevant information and/or data from published sources (*e.g*. the peer reviewed scientific literature, existing assessment, etc.), results of modelling activities that may assist the data interpretation and evaluation, or results of research activities that may be relevant to interpreting the *primary GMP data* in a valid and meaningful way (*e.g*. process studies, food-web studies, etc.). Such data will comprise an important contribution to

the Stockholm Convention evaluation process, especially in the initial period where the necessary data management infrastructure is still under development in some regions.

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

- **Un-aggregated data:** individual sample measurement values (*e.g*. the concentration of PCB153 in air, sampled at location x at time y);
- **Aggregated data:** (statistically) summarised data, *e.g*. averaged values that summarise the measurements on a number of individual samples (see Chapter 3).

6.2.2 Data policy

The GMP data handling should promote transparency of process, both with respect to the data themselves, and their treatment and analysis. A detailed description of data treatment is described in GMP DWH user guides available at www.pops-gmp.org.

The objective of the GMP data policy is also to ensure access (for the purposes of the Stockholm Convention evaluations) to the most relevant and up-to-date information available. All GMP data presented in the data warehouse are endorsed by the respective countries through the data collection process performed by the ROGs.

In considering potential public access to data, a distinction is usually made between non-aggregated data, aggregated data, and high level meta-data. Sensitivity regarding publicly available data generally decreases as follows: un-aggregated data > aggregated data > high level meta-data; where high-level meta-data are generally not subject to any access restrictions.

Part of the data generated under the GMP will already be publicly available, as they could be accessible soon after their generation. Other data, however, may be restricted; for example, subject to a moratorium to allow scientists responsible for these data to publish their results before disclosing the generated data.

Use of data for the purposes of the Stockholm Convention evaluations must not compromise the rights of the data owners. Therefore, data owners should be fully informed of how their data will be used, and what parts of data or results and when will be made public in order to ensure the owners consent. Furthermore, full and proper acknowledgement and citation of data sources is a key part of the data policy.

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

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

6.3 Data quality

Criteria for the evaluation of monitoring activities that could contribute to the Stockholm Convention global monitoring plan are set out in Annex I to the Implementation of the global monitoring plan for effectiveness evaluation as amended after the fourth meeting of the Conference of the Parties to the Stockholm Convention (UNEP/POPS/COP.6/INF/31/Add.2). All data submitted for consideration under the GMP are evaluated and validated for inclusion in the regional monitoring reports by the regional organitaion groups.

Data quality requirements shall be the same for all regions; where necessary, the objective will be to build capacity to meet the criteria set out in the GMP implementation plan.

In addition to QA/QC considerations relating to the accuracy of the results themselves, QA/QC routines need to be implemented to ensure that quality is maintained during the data exchange process. Data compilation and data reporting include a number of steps where (considerable) potential exists for

introducing errors: data entry, application of algorithms used in data conversion of transformation, data communication, etc. This is especially so when data are transferred beyond the 'horizon' of those, who are most familiar with them and therefore best placed to spot apparent discrepancies, *i.e*. those responsible for collecting/generating the data. It is therefore recommended that:

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

6.4 Data flow and storage facilities

6.4.1 Scope

The main goal of the Global Monitoring Plan data strategy is to compile un-aggregated - primary GMP data. Un-aggregated data permit data treatment in a transparent and consistent manner according to agreed assessment methodologies (see chapter 3 for more details). If these methodologies are modified or further developed at some point in the future, the availability of un-aggregated - primary GMP data provides the best possibilities for re-calculation or for repeating previous data treatment.

Aggregated data provide much more limited potential for re-analysis or for combining data from different sources. Most data derived from supplementary information will be aggregated (unless they are otherwise accessible as un-aggregated data from data centres/archives).

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

6.4.2 GMP data storage (compilation and archiving)

The Global Monitoring Plan Data Warehouse (GMP DWH) is an online tool developed for collecting, handling, long-term storage, approval and visualization of data on persistent organic pollutants (POPs) under the Stockholm Convention.

All tools and GMP DWH are available through web based user interface. The best place where to start is web portal www.pops-gmp.org. User interface of DMP DWH is embedded into this portal as well as all necessary documentation, user guides and links to all modules of the data warehouse.

The GMP Data Warehouse consists of several modules:

- Data repository:
    - Un-aggregated data repository;
    - Aggregated data repository:
    - Data access management;
    - Sampling sites management;
    - Data imports;

- Automated validations;
- Data management;
- Automated aggregation;

- Data visualization:
  - Spatial distribution;
  - Data availability;
  - Summary statistics;
  - Time series analysis;
  - Data exports / reports;
- Information web portal;
- Documentation.

A primary purpose of the GMP data warehouse is to provide transparency to the process, facilitating access to the data and results that are the basis for any conclusions of the (sufficiency and effectiveness of the) evaluations. The GMP Data Warehouse could also function as the data centre for maintaining the database of meta-data, including meta-data on GMP implementation in the various regions, and information and documentation that may be required by assessment groups concerned with, for example, data quality evaluations, such as information on laboratory performance.

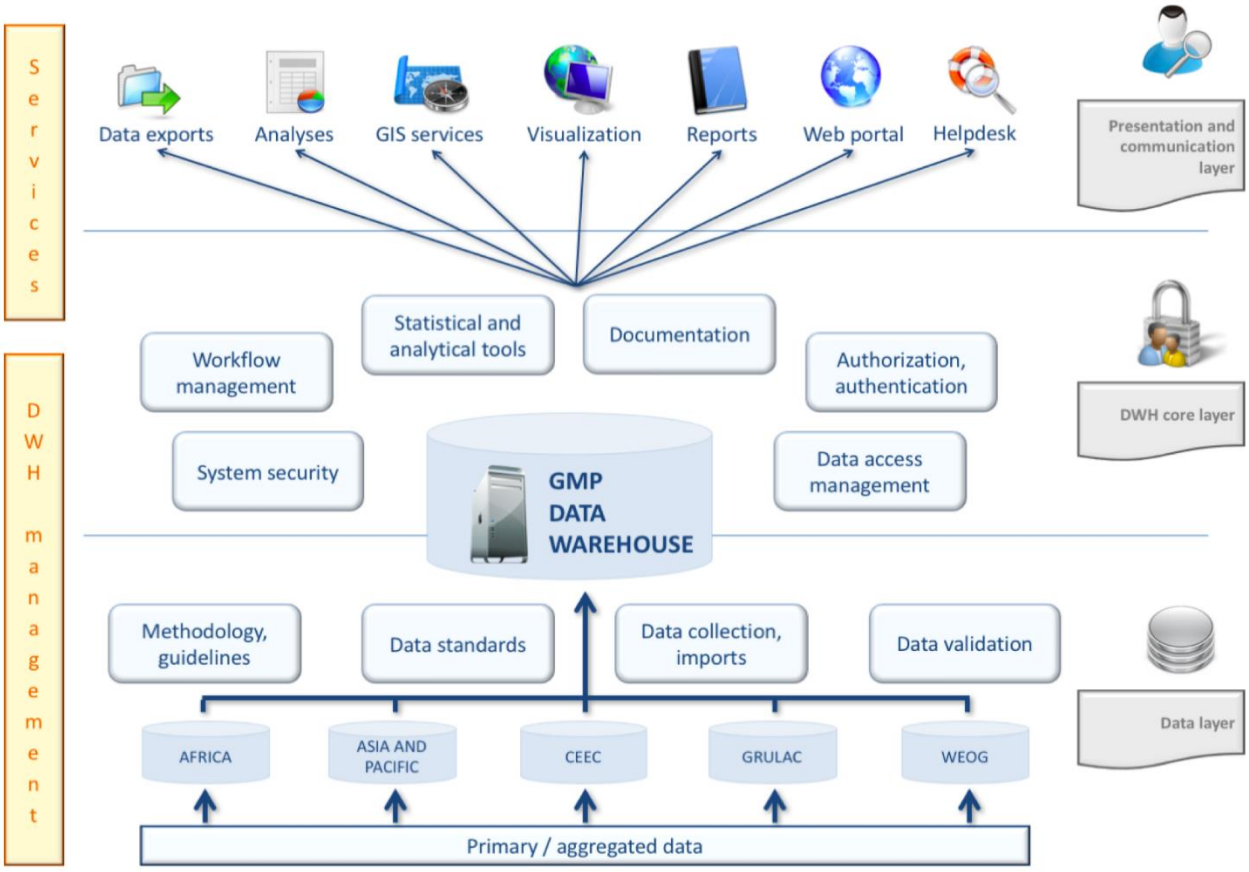


Figure 6.1: GMP Data Warehouse scheme

6.4.3 Data reporting scheme/flow

The sequence of distinct stages regarding data collection and reporting can be summarized as follows:

- Data providers (institutions operating/running individual monitoring programs or data owners) generate information and report both un-aggregated and aggregated data as well as meta data to the GMP Data Warehouse. GMP DWH serves as a regional data centre for individual ROGs;
- ROG members prepare regional reports on top of data products derived from collected data and relevant supplementary data sources;
- Based on outcomes of regional reports as well as data products of GMP DWH Global report is created and delivered to COP.

6.4.4 Data continuity

Since the overarching goal of the GMP is to provide comparative, harmonized and conclusive information on long term trends in concentrations of persistent organic pollutants in the environment, it is important to collect data in a way which allows for such interpretation of trends.

Prior each data collection phase of under the Global Monitoring Plan (e.g., in 2014 or 2018) both un-aggregated and aggregated data from previous GMP phases are copied to GMP Data Warehouse – each GMP phase contains all available and already reported previous GMP data.

- Data should be linked to previously established sampling sites using their unique identifiers whenever possible;
- Both un-aggregated and aggregated data are reported on top of previously collected data from previous phases of GMP;
- The GMP DWH is also verifying data continuity during the data input.

6.4.5 Standardized data exchange

The GMP DWH has been designed to allow for reliable collection of data on POPs concentrations in the following core matrices: air, human milk, human blood, and water. Outcomes of large established environmental monitoring programmes are preferred to be used as data sources for purposes of GMP; however national projects can also serve as sources of POPs data. Different data sources bring a high degree of heterogeneity into the data collection within the GMP phases, as each of the monitoring programmes have different objectives and performance. It is therefore essential to define a standardized format for data input to the GMP DWH, and also design and establish processes and services, which will ensure such standardized inputs, data handling and outputs for all POPs data/metadata.

Reporting of data into GMP DWH is designed in a manner that it is technically feasible and convenient to the highest degree possible for all partners concerned, minimizes the potential for errors and ensures that all reporting requirements are met; however this is a major challenge. The text below therefore outlines the core information

Data structure

All of four data collection branches contain three common data structures which have the same base and meaning but they differ a little bit among each other based on different nature of individual matrices. Basic data structures are:

Site

Site represents the place where the data were sampled. It can represent single point or even some area. Every site has its unique ID and name. By geographic coordinates a site is properly placed on the Globe and in addition there are attributes to describe and categorize a site. These attributes differs for each matrix.

Sampling attributes

Sampling attributes represents description of a sample (or all samples in case of aggregated data). Several attributes (such as year or monitoring programme) are common for all four matrix branches but there are such attributes which differs for individual matrix branch (such as sampling method for air matrix or blood source for human blood matrix).

Measurement

Measurement represents concentrations of particular chemical parameter expressed as a summary statistics value set in case of aggregated data (minimum, maximum, mean, median, no. of values) with additional description such as LOQ handling method etc. In case of un-aggregated data measurement represents individual concentration value.

Data hierarchy

Site, sampling attributes and measurement data structures extends each other and creates 3-level hierarchy as is shown in Figure 6.2 below.

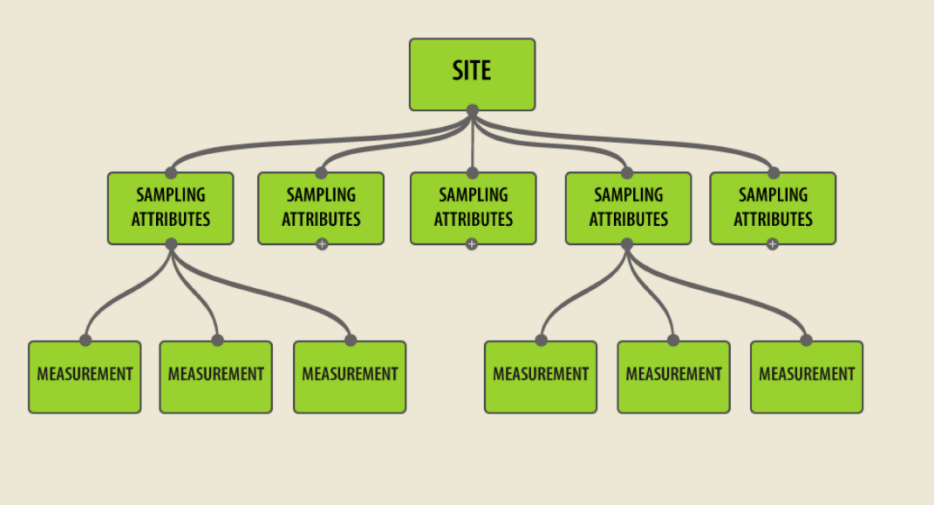


Figure 6.2: Data hierarchy

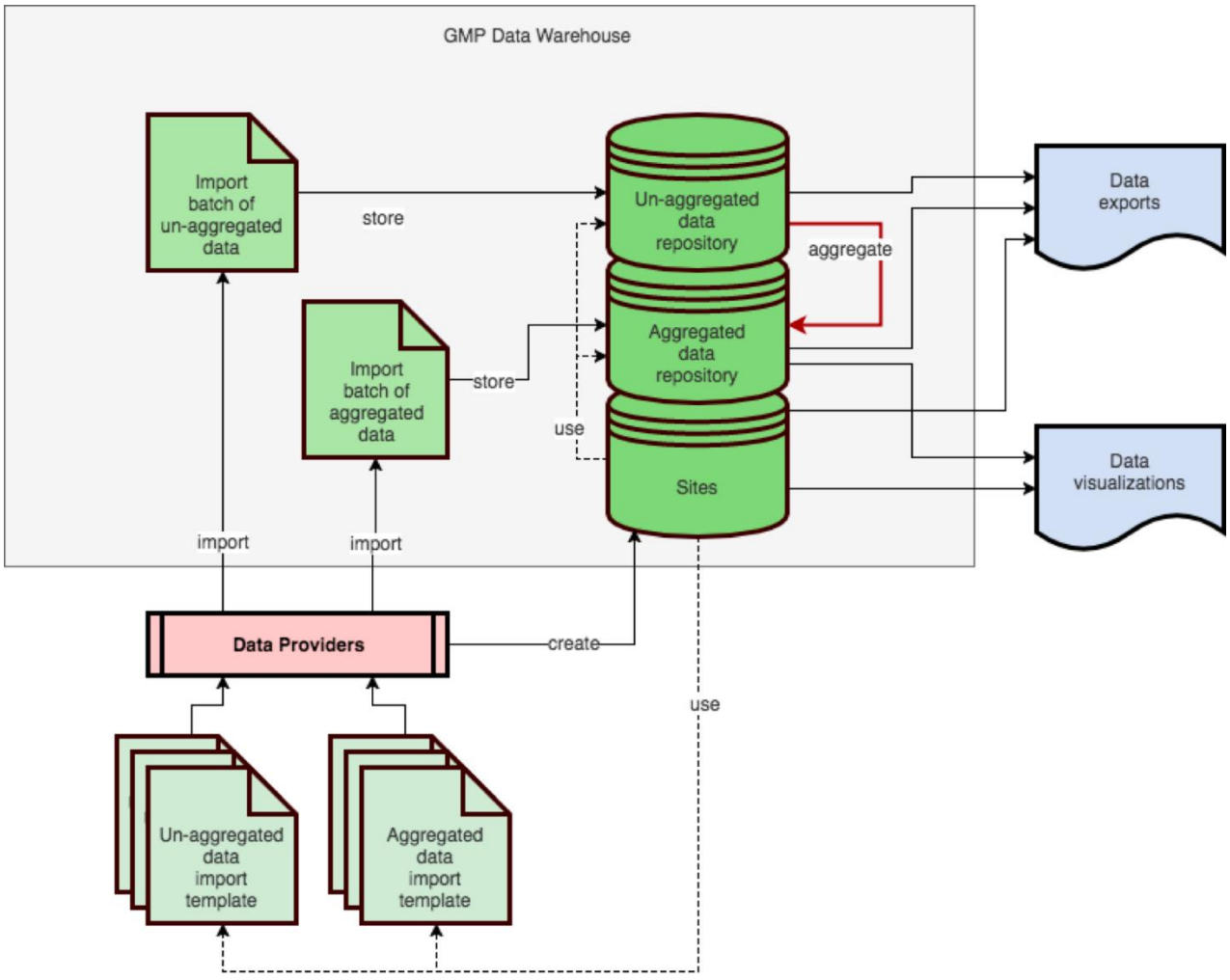


Figure 6.3: Data import process

The structure of the data fields covers important parameters that must be reported in a fully standardized and parametric way such as: geographical identification and time of reported data, "measurement – value – unit" chain and definition of data aggregation (if applied).

The following list highlights the most important data fields and information items, which are considered obligatory in the GMP DWH:

- Contact identification of the data administrator responsible for data entry;
- Identification of site reported and identification of any type of spatial aggregation (if used);
- Predefined set of reported chemicals (POPs);
- Definition of method used, including corresponding LOQ;
- Identification of units used for reported concentration values;
- Description of time aggregation (if used);
- Definition of variability (an obligatory field for aggregated data).

The list of parameters in import templates is shown in the table below:

Table 6.2: List of parameters in import templates

AIR	HUMAN MILK	HUMAN BLOOD	WATER
SITE ID (NUMBER)	SITE ID (NUMBER)	SITE ID (NUMBER)	SITE ID (NUMBER)
SITE NAME (TEXT)	SITE NAME (TEXT)	SITE NAME (TEXT)	SITE NAME (TEXT)
LONGITUDE (NUMBER)	REGION (CODE LIST)	REGION (CODE LIST)	REGION (CODE LIST)
LATITUDE (NUMBER)	COUNTRY (CODE LIST)	COUNTRY (CODE LIST)	COUNTRY (CODE LIST)
REGION (CODE LIST)	YEAR (NUMBER)	YEAR (NUMBER)	SURFACE WATER TYPE
COUNTRY (CODE LIST)	START OF SAMPLING (NUMBER)	START OF SAMPLING (NUMBER)	LONGITUDE (NUMBER)
SITE TYPE (CODE LIST)	END OF SAMPLING (NUMBER)	END OF SAMPLING (NUMBER)	LATITUDE (NUMBER)
POTENTIAL SOURCE TYPE (CODE LIST)	TYPE OF SAMPLE (CODE LIST)	BLOOD SOURCE (CODE LIST)	REGION (CODE LIST)
YEAR (NUMBER)	MONITORING PROGRAMME/NETWORK (TEXT)	FRACTION (CODE LIST)	COUNTRY (CODE LIST)
START OF SAMPLING (NUMBER)	CHEMICAL – GROUP (CODE LIST)	MONITORING PROGRAMME/NETWORK (TEXT)	OCEAN OR SEA (CODE LIST)
END OF SAMPLING (NUMBER)	PARAMETER (CODE LIST)	CHEMICAL – GROUP (CODE LIST)	SITE TYPE (CODE LIST)
TYPE OF SAMPLING (CODE LIST)	METHOD (CODE LIST)	PARAMETER (CODE LIST)	DISCHARGES (CODE LIST)
TYPE OF PASSIVE SAMPLING (CODE LIST)	LOQ (NUMBER)	METHOD (CODE LIST)	YEAR (NUMBER)
RECALCULATION (CODE LIST)	NO. OF VALUES (NUMBER)[A]	LOQ (NUMBER)	START OF SAMPLING (NUMBER)
CALIBRATION DESCRIPTION (TEXT)	NO. UNDER LOQ (NUMBER)[A]	NO. OF VALUES (NUMBER)[A]	END OF SAMPLING (NUMBER)
MONITORING PROGRAMME/NETWORK (TEXT)	VALUE (NUMBER)[P]	NO. UNDER LOQ (NUMBER)[A]	TYPE OF SAMPLING (CODE LIST)
CHEMICAL – GROUP (CODE LIST)	VALUE (MEAN) (NUMBER)[A]	VALUE (NUMBER)[P]	DEPTH (NUMBER)
PARAMETER (CODE LIST)	VALUE (MEDIAN) (NUMBER)[A]	VALUE (MEAN) (NUMBER)[A]	TEMPERATURE (NUMBER)
METHOD (CODE LIST)	MINIMUM (NUMBER)[A]	VALUE (MEDIAN) (NUMBER)[A]	SALINITY (NUMBER)
LOQ (NUMBER)	MAXIMUM (NUMBER)[A]	MINIMUM (NUMBER)[A]	MONITORING PROGRAMME/NETWORK (TEXT)
NO. OF VALUES (NUMBER)[A]	5TH PERCENTILE (NUMBER)[A]	MAXIMUM (NUMBER)[A]	CHEMICAL – GROUP (CODE LIST)
NO. UNDER LOQ (NUMBER)[A]	95TH PERCENTILE (NUMBER)[A]	5TH PERCENTILE (NUMBER)[A]	PARAMETER (CODE LIST)
VALUE (NUMBER)[P]	SD (NUMBER)[A]	95TH PERCENTILE (NUMBER)[A]	METHOD (CODE LIST)
VALUE (MEAN) (NUMBER)[A]	LABORATORY (TEXT)	SD (NUMBER)[A]	LOQ (NUMBER)
VALUE (MEDIAN) (NUMBER)[A]		LABORATORY (TEXT)	NO. OF VALUES (NUMBER)[A]
MINIMUM (NUMBER)[A]			NO. UNDER LOQ (NUMBER)[A]
MAXIMUM (NUMBER)[A]			VALUE (NUMBER)[P]
5TH PERCENTILE (NUMBER)[A]			VALUE (MEAN) (NUMBER)[A]
95TH PERCENTILE (NUMBER)[A]			VALUE (MEDIAN) (NUMBER)[A]
SD (NUMBER)[A]			MINIMUM (NUMBER)[A]
LABORATORY (TEXT)			MAXIMUM (NUMBER)[A]
			5TH PERCENTILE (NUMBER)[A]
			95TH PERCENTILE (NUMBER)[A]
			SD (NUMBER)[A]
			LABORATORY (TEXT)

[A] – THE ITEM IS VALID FOR AGGREGATED DATA REPORTING ONLY

[P] – THE ITEM IS VALID FOR PRIMARY DATA REPORTING ONLY

Data validation

The ROGs are responsible for validating all data that will be included in the regional monitoring reports and in the GMP DWH. Each (completed/filled) record must therefore contain all required information, i.e., relevant unit as an obligatory attribute of a concentration value. Imported data fields have predefined form and are either text, number or item selected from a particular code list. Automatic validations are inseparable part of data import process to the GMP DWH. Only fully validated data can be used for further processing.

Security rules and principles of the DMP DWH are designed to reflect and support whole process of GMP data collection and report assessment – both the regional and global levels. Important rule of thumb is to allow individual data providers and ROGs to work with GMP data simultaneously but independently without interference each other.

All data are approved by ROGs. General rules applied are as follows:

- Data provider can import data;

- Data provider can verify its own data;
- Data provider can delete its own data;
- Data provider can see data within a ROG he/she belongs to;
- Data provider can manage all sites within his/her ROG;
- ROG can see data within its ROG;
- ROG can approve verified data;
- GCG can publish approved data.

Detail description of security and user access management is described in technical documentation of GMP DWH and is available on the GMP website.

6.4.6 Data products

The GMP Data Warehouse provides several forms of data exports, reports and visualizations generally called data product. Form and shape of individual data products should be compatible with requirements on regional and global monitoring reports introduced in Chapter 7.

6.5 Data analysis

To promote comparability of POPs data collected in different the regions, harmonized assessment tools (such as statistical methods for temporal trend evaluations) are available in GMP DWH. GMP output products represent maps, tables and charts that can be directly used in regional reports.

The reliable identification of trends including statistical evaluation is carried out on all data in GMP. Details on data the data treatment are provided in Chapter 3. Trends identified are site-specific.

7 STRATEGY, PROCESS AND DRAFT STRUCTURE FOR REGIONAL MONITORING REPORTS

7.1 Implementation of the global monitoring plan for effectiveness evaluation

The implementation arrangements are set out in the implementation plan for the global monitoring plan for effectiveness evaluation (UNEP/POPS/COP.6/INF/31/Add.2). The implementation plan outlines the main tasks that must be completed in relation to implementation of the global monitoring plan for the first and subsequent effectiveness evaluations. The Conference of the Parties has determined that the minimum requirements for effectiveness evaluation are that:

- The status quo as of the date on which the Convention or its amendments entered into force is generally used as the baseline. If such information is not available (for instance monitoring data on certain POPs are not available at the date of entry into force), the first relevant information which becomes available is considered as the baseline against which changes over time are evaluated;
- Air monitoring and human exposure through human breast milk or human blood are used as core data;
- Water is the core environmental matrix for monitoring PFOS;
- Such comparable and representative core data should be obtained from all five regions;
- Guidance on standardization should be updated as needed;
- The strategic arrangements and partnerships established in the first evaluation should be maintained and extended, as appropriate.

The arrangements for obtaining comaparable and consistent monitoring data described in the implementation plan cover the following:

- The identification and evaluation of potential sources of core media data for the monitoring report for effectiveness evaluation, including the definition and use of criteria to evaluate monitoring activities that can contribute to the global monitoring plan;
- The strategic arrangements and partnerships for the acquisition of core media data for the monitoring reports;
- The modalities for summarizing and presenting monitoring data on a regional basisfor use in effectiveness evaluations, including reporting on regional and global transport.

Further details can be found in document UNEP/POPS/COP.6/INF/31/Add.2 available at http://chm.pops.int/Implementation/GlobalMonitoringPlan/Regionalorganizationgroups/tabid/179/Default.aspx.

7.2 Outline of regional monitoring reports (to be modified for the use in the particular regions as appropriate)

According to its terms of reference (annex to decision SC-8/18), the main objectives of the regional organization groups are to define and implement the regional strategy for information gathering, including capacity building and establishment of strategic partnerships in order to fill the identified data gaps (see section 7.1 above), and to prepare the regional monitoring reports as input to the global monitoring report for effectiveness evaluation.

The annotated outline of the regional monitoring reports is set out below.

Acknowledgements

Preface

Abbreviations and acronymes

Glosary of terms

Executive summary

I. Introduction

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

II. Description of the region

Describes:

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

III. Organization

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

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

Strategy for using information from existing programmes

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

IV. Methodology for sampling, analysis and handling of data

Strategy for gathering new information

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

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

Strategy concerning analytical procedures

A brief description of analytical procedures used to ensure quality and comparability of data includes:

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

Strategy concerning participating laboratories

A description of the strategy regarding participating laboratories includes:

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

Data handling and preparation for the regional monitoring report

A description of the strategy for data handling and for developing the regional monitorning reports includes:

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

V. Preparation of the monitoring reports

This section includes:

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

VI. Results

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

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

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

The results in context

The first global monitoring reports set a baseline for information on levels of persistent organic pollutants in humans and the environment. The data available for each region vary greatly, with some regions having considerable historical data. Under the effectiveness evaluation the global progress achieved under the Convention will be evaluated. For that reason, in most cases the status quo as of the date on which the Convention or its amendments entered into force will be used as the baseline to evaluate its effectiveness on the global level. If such information is not available (e.g., monitoring data) the first relevant information which becomes available will be considered as the baseline against which changes over time will be evaluated.

Review of levels and trends in the regions

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

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

Information concerning long range transport

Infromation concerning long range transport should be included depending on availability of information at the regional scale.

VII. Conclusions and Recommendations

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

7.3 Outline of the global monitoring report

According to its tems of reference (Annex to decision SC-8/19) the main objective of the global coordination group is to assist the Secretariat in coordinating and overseeing the implementation of the global monitoring plan and to produce the global monitoring report, as major input for effectiveness evaluation under Article 16 of the Stockholm Convention. The global monitoring report is to be based on the five regional monitoring reports, while syntethising and presenting the regional information from a global perspective.

The global coordination group is further requested to evaluate the arrangements for the global monitoring plan at the end of each evaluation phase and develop recommendations for consideration by the Conference of the Parties.

The outline of the global monitoring report addresses both of these aspects as well as the various other tasks performed by the global coordination group that are listed in the terms of reference:

Acknowledgements

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Abbreviations and acronymes

Glosary of terms

Executive summary

I. Introduction

II. Results of the Global Monitoring Plan

1 Data availability

2 Data consistency and comparability

3 Data handling

4 Monitoring results

4.1 Air

4.2 Human matrices

4.3 Water

4.4 Other media

5 Long-range transport

III. Evaluation of the global monitoring plan and conclusions and recommendations for the next phase

1 Arrangements

2 Challenges to implementation

All chapters will be organized according to the following internal structure (as approppriate):

Introduction

Overview

Main findings

Conclusions and recommendations

The executive summary will follow the outline of the full report and will reproduce the respective main findings as well as conclusions and recommendations.

8 ENVIRONMENTAL SPECIMEN BANKING

8.1 Introduction

Environmental Specimen Banking is an activity to collect and keep "representative" environmental and human samples (specimens) for long-term, typically several decades, without changing their chemical compositions and properties, including a variety of pollutants accumulated in the specimens (Becker, et al., 2006). "Representative" means well-described environmental samples commonly or widely present in the environment so that temporal and / or spatial trends will be revealed by the analysis of the pollutants in the archived samples in future. Selection and collection of environmental samples should be designed carefully so that a minimum set of archived samples will provide an unbiased view of the levels of pollutants in specified environment. The sampling design may need to address several factors, including types and amounts / number of samples to be collected and archived, sampling locations, frequencies, seasons, and methods, etc., that will be optimally selected by reflecting information on major sources of target POPs, their transport and bioaccumulation processes as well as feasibilities and cost-effectiveness, etc. This is basically the same procedure as to design and conduct environmental monitoring itself (see Chapter 3 Statistical Considerations, and Chapter 4 Sampling and Sample Preparation Methodology). The activity also needs a special facility for archiving samples for long-term, i.e., environmental specimen bank. As Environmental Specimen Banking is aiming to support not only the present but also future monitoring activities under the Convention as described later, the banking activity is expected to have a wider scope than that covered under the present global monitoring plan, GMP.

Environmental Specimen Banking has been playing a vital role in many countries as an indispensable tool to support both basic science and decision-making processes on various environmental issues, particularly chemical pollutants. There are many environmental specimen banking programs in the world. Some have long histories, conducted with long-term monitoring, and archive specimens back to late 1960's / early 70's (for example, Swedish Museum of Natural history, and National Aquatic Biological Specimen Bank / National Wildlife Specimen Bank in Canada). In the middle 70's, US and Germany started pilot Environmental Specimen Banking activities (NIST's National Biomonitoring Specimen Bank and Germany's Federal Environmental Specimen Bank, respectively) as a bilateral program and shifted to long-term phase later. In Japan two environmental specimen banks are operating with archived specimens back to 60's (es-BANK in Ehime Univ.) or 70's (Environmental Time Capsule in NIES). After 80's the number of banks has been increasing, including Nordic ESB (Norway, Finland, Denmark, Faroe Island), France (IFREMER, ANDRA), UK (Fish), China (Yangtze ESB), Italy (Antarctic Environmental Specimen Bank, The Mediterranean Marine Mammal Tissue Bank), Republic of Korea (NIER), Spain (Biscay Bay Environmental Biospecimen Bank). There are many environmental specimen banks that also include human samples, among which some have been operated for human biomonitoring of chemical exposure (for example, Wiesmüller et al., 2007). As an outcome of a series of symposiums, workshops, and meetings on Environmental Specimen Banking, the International Environmental Specimen Banking (IESB) Group was established as a forum for the information exchange and promotion of the activities (http://www.inter-esb.org/index.html)

Many of the above institutions have their own homepages to describe their ESBs and show their activities, including archived samples, major scientific findings and research papers. Please see the links in the above homepage of IESB for more details of each Environmental Specimen Banking activity.

Environmental Specimen Banking is expected to play a key role to support POPs monitoring under the GMP of Stockholm Convention (UNEP/POPS/COP.4/31). By the systematic storage of part of the environmental samples collected for monitoring purpose, each Party will be able to analyze the samples in the future in order to obtain baseline data for newly added POPs, to reveal temporal and / or spatial trends of POPs / newly listed POPs / POPs candidates, to identify emerging pollutants, to assess the quality of the previous analytical data, and to get quantitative data for previously "not detected" or unattended compounds by more advanced analytical methods. As an example, Figure 8.1 shows temporal trends of PFOS and other

perfluorinated surfactants levels in mother's milks from Stockholm, Sweden, which were archived in a specimen bank at the Swedish Museum of Natural History (Sundstrom et al. 2010). Temporal / spatial trend data will be very helpful in the review process of proposed chemicals to the annexes of the Convention, and in the effectiveness evaluation process. Furthermore it is expected to support implementation of the Convention, particularly in developing countries, by realizing earlier start of the sample collection and storage while the analysis will be conducted after the relevant capacity building / enhancement procedure will be completed. In fact, in UNEP/GEF-GMP-2 programme, which supports data collection of POPs in human breast milk in order to support effectiveness evaluation of the Convention, part of pooled milk sample from each country is archived in WHO Global Human Milk Bank for future new POPs analysis while part of individual sample is planned to be archived in each Party for analysis by country (Malisch et al., 2017).

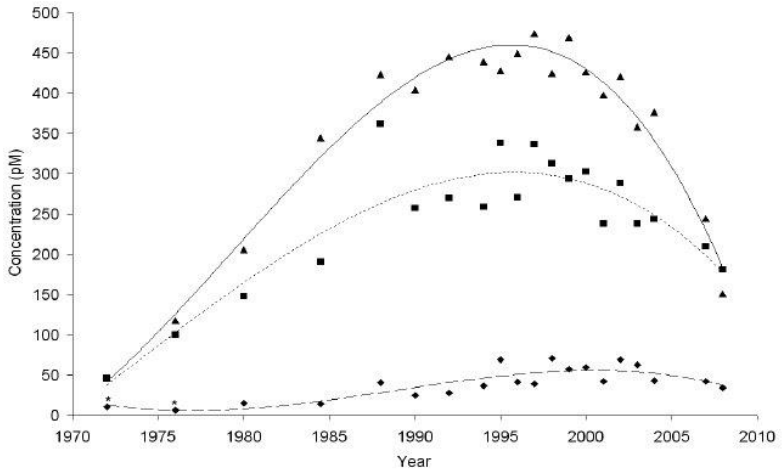

Figure 8.1: Concentration (pmoles/ml) of PFOS, PFOA and PFHxS in mother's milk from Stockholm 1972-2008 (Sundstrom et al. 2010).

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

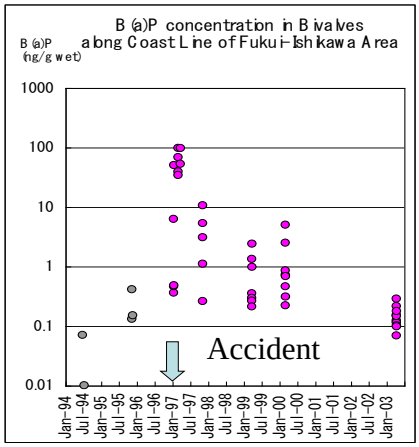

Figure 8.2: Benzo(a)pyrene levels in bivalve samples collected along Japanese coastline before and after a tanker accident (Jan 1997) (Shibata, 1998)

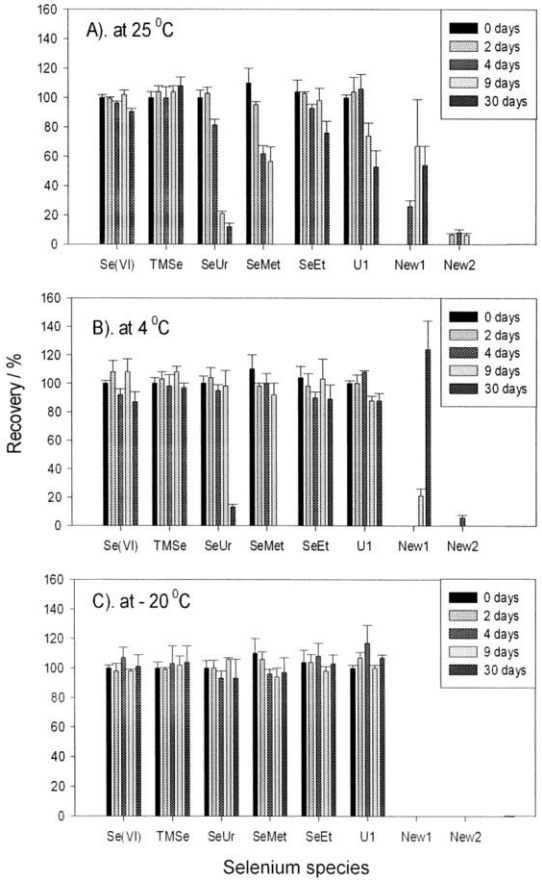

Figure 8.3: Stability of organoselenium compounds added to human urine at different temperatures. Selenourea was found to be least stable among the Se-compounds examined, but could be kept intact for 30 days at -20 C (Zheng et al 2002).

Many of the Environmental Specimen Banking programs have high capacity and capability to produce large amount of homogeneous materials in terms of chemical composition as well as to analyze variety of pollutants, and are sometimes accompanied with the production of reference materials for QA/QC of the environmental analysis (for example, National Institute of Standards and Technology, USA (NIST), and National Institute for Environmental Studies, Japan (NIES), produce a series of SRMs / CRMs for QA/QC). Thus the Environmental Specimen Banking is expected to support GMP of the Stockholm Convention not only by archiving monitoring samples but also by building / enhancing analytical capacity.

8.2 Basic concept and requirements

8.2.1 Basic concept of environmental specimen banking

Environmental Specimen Banking is a highly conserved operation to be continued for long term without changing fundamental procedures in order to secure sample comparability and chemical properties / integrities. Therefore the whole procedure, including the type of samples collected, sampling locations, sampling intervals, amount of sample archived, container type used for archival, transport of samples, sample homogenization and processing, homogeneity determination, , sub-sample portioning, storage method, and storage facility maintenance should be carefully designed, operated and recorded. Detailed description of each procedure, manuals or SOPs for the sample collection, processing, and storage procedure, and periodical updating of these manuals are necessary for the proper operation of a specimen

bank facility. The stored samples should also be accompanied with enough supplemental information for later statistical analysis and interpretation of the results as well as for ensuring “traceability”. Quality and quantity of accompanied data will change the value of the archived sample (Table 8.1).

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

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

8.2.2 Samples to be stored

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

Environmental monitoring may include several different concepts; i.e., to know concentration of pollutants in different environmental compartments (to know sources, levels, and chemodynamics of pollutants, or to check compliance with environmental quality criteria / standards), to reveal exposure status (exposure monitoring for risk assessment and control), and to evaluate adverse effects of pollutants to wildlife / human beings (effect monitoring) (see, for example, Rüdel et al. 2009, for concepts of environmental monitoring). Biological samples are preferred for banking because they tend to bioaccumulate chemicals like POPs in higher concentrations through food web, and also their POPs levels tend to be smoothed over time due to long half-life of POPs within the body. Thus a small amount of biological samples collected once a year, for example, may provide us with representative levels of POPs (pollution levels, or exposure status) in an area each year, provided that well designed sampling protocol is taken to minimize effects of variation other than the environmental level, such as species, sex, age, size, season etc.. If instead water or air samples are collected, a much larger amount of samples collected frequently in short interval will be needed to get comparably reliable view of their environmental levels and the temporal trends. In addition, biological samples will potentially provide us with information on the effects of pollutants to wildlife / human beings, i.e., suitable for effect monitoring.

Biological samples for the banking may be classified into the following three groups; 1) common, short-lived organisms in lower trophic level, such as fishes and bivalves, which are suitable for revealing detailed spatial / temporal trend analysis, 2) long-lived, higher-trophic level organisms, typically top-predators like fish-eating birds (or their egg contents) and marine mammals (or their tissues obtained from live / dead animals), which are sentinel species to POPs by accumulating them higher than other species in lower trophic levels, and 3) human samples. Group 1) will be useful for periodical (yearly) monitoring of pollution

status to know their temporal trends, while Group 2) may represent a highest level of POPs pollution in a selected ecosystem / environment and thus will be suitable for assessing their ecological risks. Human data will primarily be used for assessing exposure to and risk of chemicals to humans and to identify priorities in regulation. Other types of specimens for the banking include soil, vegetation, and environmental samples with annual ring / layer structure such as sediment core and trunk of trees (Becker et al, 2006, and references therein), and bark pocket of trees as a time capsule for the past environment (Satake et al., 1996). Time-integrated type of air or water samplers, such as passive air sampler, may alternatively be collected and kept for the purpose (Table 8.2).

Table 8.2: Samples suitable for banking.

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

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

8.2.3 Long-term storage method

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

There are apparently no general criteria of the storage temperatures for the bank, though several different temperatures have been selected for different purposes (Table 8.3). Generally speaking, samples will be kept better under lower temperatures (Zheng et al., 2002). Biological samples at liquid nitrogen temperature (–196 °C), or in liquid nitrogen vapor phase storage facility (around –150 to –160 °C), will be stable and chemically unchanged for decades while those kept at –20 °C tend to be deteriorated to some extent in decades as desiccation and metabolic degradation are not ignorable at the temperature. Deep freezer at –80 or –85 °C, the temperature originally selected for storing dry-ice, have been used extensively in many banks and for other purposes, and are proven to be useful for the long-term preservation of many types of samples. Another temperature, around –60 °C, is frequently used commercially for the large-scale storage of fishes

and meats, and is proven to be also useful for long-term storage of biological samples. Techniques for construction and maintenance of large refrigerated warehouses under –60 °C have been established, and a large capacity of this type of storage is available now around fishing ports / air ports / other hub of transports in the world.

Table 8.3: Typical temperatures used for banking of specimens.

Room Temperature	**Dry samples (soils, vegetation, bird egg shells, hair, etc.)**
4 degrees of Celcius (refrigerator, cold room)	**Dry samples, water**
-20 / -25 degrees of Celcius (freezer, freezing chamber)	**Biological samples, sediments etc. for heavy metals, POPs analysis (not suitable for long-term storage)**
-60 / -90 degrees of Celcius (deep freezer, deep freezing chamber)	**Biological samples, sediments for long-term storage; useful also for biochemical analysis**
-160 / -196 degrees of Celcius ((vapor phase) liquid nitrogen freezer)	**Biological samples; chemically most appropriate for long-term storage**

It has, however, to be considered that electric freezers will need costly regular maintenance of the mechanical refrigeration parts (Owen and Woods, 2008). Furthermore, measurable recrystallization processes within water may occur at temperatures above –130 °C (Eisenberg and Kauzmann, 2005). Therefore, the best available method is to keep samples under vapor phase of the liquid nitrogen because of the lower temperature (typically around –150 to –160 °C) under oxygen-free condition. Though such a system tends to cause high investment costs, it may be cost-effective in the long run, depending on the amount of stored samples and availability of liquid nitrogen and its cost. In addition, the liquid nitrogen cooling system will keep samples at low temperature more robustly / securely than electric freezers / cold rooms at the time of disaster. At the Great East Japan Earthquake in March 2011, loss of electricity for three days threatened the archived samples in the environmental specimen bank at the National Institute for Environmental Studies, Japan (Karube et al, 2015). The temperatures of all vapor-phase liquid nitrogen freezers were kept at –160 °C due to remaining liquid nitrogen in the bottom of the tanks and their vacuum isolation, while the temperature of large cold rooms operated at –60 °C gradually increased but still kept below –47 °C after three days. The temperatures of –80 °C freezers, on the other hand, increased to nearly zero °C only after a day after the electricity shut down, and dry-ice blocks had to be put into the freezers every day during the period of electricity loss in order to keep the samples frozen. It is important to set up emergency operational procedures in order to keep samples against such rare but disastrous events.

Note that sample storage for chemical analysis reported in this chapter is different from storage of cells / genes for medical or livestock application where cell viability rather than chemical integrity is of prime concern.

8.2.4 Facility requirement

Environmental Specimen Banks may consist of low temperature storage facility, sample processing room, sample analysis room, and data storage and analysis facility. To ensure secure long term storage of valuable samples, arrangement of some back-up systems, like extra storage facility needed for accidental trouble of the used freezers, and back-up electric generator or CO2 / liquid nitrogen (LN2) supply line against a short term electricity shutdown, are vital. Size and temperature of the storage facility (from a single freezer to several large cold rooms or a series of liquid nitrogen freezers) is highly variable according to the type and amount of collected samples for storage, and / or available resources. It should be noted that even a couple of freezers will be very useful and play important role together with well-designed environmental monitoring activity, especially for human bio-monitoring where limited amount of valuable human samples,

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

It is also recommended to have sample analysis capability together with storage and processing facility in order to regularly check homogeneity of the samples in case of homogenized sample storage, "cleanness" of the facility, and ensure "free of contamination" during sample collection, transport, processing and archiving. Homogeneity is properly assessed by chemical analysis. It is checked in two ways, i.e., within a bottle and between bottles, typically by the analysis of several elements, including minor and trace ones. As for contamination check during the sample handling, many different chemicals may be analyzed, and a series of analytical instruments are required for proper operation of the facility. Laser-diffraction particle size analysis (PSA) can also measure the equivalent spherical diameter in an average volume distribution so that during sample processing, measurements can be made to determine particle size distribution, homogeneity of size, and track particle size as a process control indicator. Alternatively, archiving individual organisms or tissues without homogenization also has marked merits as for available information in future retrospective analysis.

Chemicals of concern for environmental / human monitoring may include many industrial chemicals, such as surfactants (including PFOS), flame retardants (including brominated flame retardants) and other plastic additives, which have been used extensively in the production of many commercial products in laboratory environment and ordinally life. It should be noted that there are many chances of contamination by these chemicals during sampling, transport and processing before final start of long term storage, and careful and regular monitoring of the whole process is very helpful for meaningful retrospective analysis in future. Some example of contamination include; elements (alkali metals, boron, arsenic etc.) from glassware, perfluoroalkyl carboxylic acids from fluoropolymer products, materials (such as bisphenol A) or additives (such as phthalate esters, alkylphenol ethoxylates) or flame retardants (such as polybromodiphenylethers, polybromobiphenyls, chlorinated paraffins, organophosphorous compounds, antimony, etc) from plastic wares, furniture and construction materials of the building. It is recommended that some "blank" samples, for example purified water, for checking whole contamination during sampling, transport and processing, will be analyzed and also stored periodically together with environmental samples, so that chemicals found in a future retrospective analysis can be assured to be originally contained within a sample rather than added, or produced, during sample handling procedure (Karube et al., 2015). Some ESBs have passive samplers in the ESB rooms where the samples are processed and store the passive samples together with the samples.

8.2.5 Administrative system

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

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

of the program. It is also important to accumulate and keep tracking analytical data of archived samples over long.

8.2.6 Safety caution and training

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

In addition to keeping good ventilation, oxygen sensor – alarm combination is recommended in a cold room, or other places, such as sample processing room, where large emission of CO2 or N2 is anticipated. Never touch frozen samples / containers / walls / shelves with naked hand / other part of skins directly.

When you touch them with your wet hand, the moisture on the hand is frozen and fixes your hand to the cold surface, thereby damaging your skin severely. Also some dangerous chemicals, such as strong acids, methanol and other organic solvent with either toxicity or flammability, may be regularly used during the operation. The handling of these chemicals, including waste management, should follow the established scheme in each laboratory, and prior and regular training / teaching of the technical person together with the regular health check on the relevant terms should be conducted to prevent accident and ensure the sustainability of the program.

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

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

8.2.7 Sample access / discarding policy

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

8.2.8 Guideline, banuals and standard operational procedures

Many Environmental Specimen Bank facilities have written Standard Operational Procedure (SOPs) for the sampling and / or storage procedures, and some are made available through websites or other means. The International Society for Biological and Environmental Repositories (ISBER) provides an international forum that addresses the technical, legal, managerial, and ethical issues relevant to repositories associated with biological and environmental specimens. Through member contributions, ISBER has developed and published the 4th edition of "ISBER Best Practices: Recommendations for Repositories" (Campbell, et al., 2018). The document provides a practical guide and suggested 'best practices' from repository professionals for the management of specimen collections and repository facilities.

8.3 Sampling and storage

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

8.3.1 Sampling devices

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

Air and water samples themselves are generally not suitable for banking due to large volumes necessary for trace pollutant analysis as well as suspected instability of chemicals that might be lost by adsorption to container wall etc. during long-term storage. Some archiving activities of these matrices have been seen in special cases, for example Cape Grim Air Archive, in which air samples have been kept in flasks for major, minor, trace gases as well as stable VOCs analysis (O'Doherty et al, 2009). Usually, however, the filters, adsorbents, or extracts, may be more suitable for future retrospective analysis of chemicals. An illustrative example is monthly collection and archiving of airborne particulate matters on quartz fibre filter collected in central Tokyo; the archived filters were used to reveal temporal trends of dioxins (Matsumura et al, 2003) and polycyclic aromatic hydrocarbons (Ezoe et al, 2004) for two decades from 1980. In a passive air sampling programme (GAPS), the extracts from the adsorbents were divided into two and one part was kept in sealed glass ampules for future retrospective analysis. Duplicate sampling by passive air sampler and archiving a set of adsorbents may be an alternative choice. Detailed record on the sampling dates, storage devices, materials used, etc., should be kept together with the samples. Filters and adsorbents should be pre-cleaned according to the sampling SOPs. It should be noted that even sampling device, such as high volume air sampler, might cause unexpected contamination from the materials used to construct the device; typical examples are perfluorochemicals in fluoropolymer products / coatings, and flame retardants and their impurities used for plastic / elastomer products (Takasuga et al., 2012).

8.3.2 Sample processing and archiving

In the case of human breast milk or blood samples, several portions of a sample will be kept in the storage tubes after gentle mixing procedure. Sample size will depend on the situation, but will be minimized but sufficient for one-time analysis of some particular chemicals/elements. Careful statistical consideration will help to determine the minimum number of individual samples for detecting temporal trends efficiently (Bignert et al., 2004).

Note that freezing process may cause precipitation of some materials, including fats, or hemolysis, which might affect homogeneity of the sample at the time of portioning. In some cases, sample processing for banking might involve separation of specimen components, such as plasma or sera for the analysis of organic contaminants, from the whole samples, like whole blood for the analysis of trace elements. In such cases, care should be taken not only to assure sample homogeneity but also to prevent / minimize contamination of target chemicals during the process (see 8.3.1). Pooled human samples are thought to represent pollution status of a population in an area, and are very efficient in terms of both the analytical costs and the banking facility. Aliquots of pooled human breast milk samples collected and analyzed at the 1st effectiveness evaluation procedure (joint WHO/Stockholm Convention programme) were kept in a freezer and are now used for the analysis of additional newly listed POPs. Pooled samples, however, have disadvantages compared with individual samples (see Chapter 3.5; Bignert et al.,.2014).

In the case of biological and soil/sediment samples, homogeneity is an important feature of the archived samples to ensure that future analysis of a small portion of the sample will provide “representative” information on the pollution status of the period. Variety of homogenizing techniques have been developed and applied to the Environmental Specimen Banking activities, including mixer, blender, chopper, crusher, ball mill, rod mill, and cryo-homogenization. Usually a hard material, such as metals and ceramics, is used for crushing/ homogenization procedures. In some cases, plastic materials, like fluoropolymers, have been used as a cover or coating material for mills. It should be kept in mind, however, that homogenization step itself may cause contamination of samples by the materials for homogenization. Even a hard metal, such as stainless steel or titanium, could be scratched off and be contaminated into the homogenized samples during mechanical homogenization step (Karube et al., 2015). Fluoropolymers have been selected to prevent contamination by metals and most POPs during homogenization, although fluoropolymers themselves may cause contamination by some organic materials including perfluorooctanoic acid (PFOA) (Lynch et al., 2018).

Both glassware and plastic tubes have been used for sample storage vessels. They should be carefully pre-cleaned before sample storage. Although glassware is easier to clean organically and has been preferred for samples to be used for organic analysis, care should be taken to prevent break because volume of water (bloods, milk) increase substantially when frozen. Glassware may not hold up to an extreme cold temperature like -160 °C, or may be broken by a rapid temperature change in a short time. Broken glass might cause injury and accidental infection when blood samples were stored. The vessels should be tightly capped. Metal screw cap or other loose cap might cause spill of liquid samples before freezing and desiccation of biological tissues during long-term storage under –20 °C or higher. In the case of glass tube, plastic caps with inner elastomer covered with PTFE or other fluoropolymer is commercially available. Although fluoropolymer is chemically stable and durable, it contains perfluorinated chemicals, typically PFOA or PFNA, and this type of cap is not suitable for their analysis. A plastic cap tightly sealed without inner elastomer is preferred. Alternatively thin foil made of aluminum is sometimes used to cover the bottle mouth to prevent direct contact between the samples and inner elastomer of the cap. It should be pointed out that aluminum foil is not organic contaminants free; its surface is apparently coated with some organic materials and sometimes low levels of target chemicals, including fluorinated chemicals, are detected. Baking foils together with glassware will be effective to minimize contamination levels. Extracts (organic solvents) from filters or other adsorbents should be kept in pre-cleaned, amber glass ampule sealed with inert gas, such as nitrogen or argon. Filters or other adsorbents will be covered with baked aluminum foil, be put into a zipped plastic bag (usually thin polyethylene bag), and be archived preferably in a freezer for

future organic analysis. It is recommended to archive blank (unused) filters together with samples in order to check the occurrence of contamination within the material / during the storage.

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

8.3.3 QA/QC and security

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

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

8.4 Communicating results to decision-makers, science and public

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

8.5 Available information on environmental specimen banking

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

Each bank has its own purpose and specific character, and has a different size and history. Variety of their experiences will be useful for setting up a new bank in a country / region where no Environmental Specimen Bank-related activities have been present. The information on their activities is available in scientific literatures (see, for example, references cited in Becker et al., 2006, which includes publications on the previous scientific meetings on the environmental specimen banking), and also their homepages. SOPs of German, Sweden and US banks are available, together with list of homepages of major Environmental Specimen Banks in the world, in the homepage of IESB (http://www.inter-esb.org/index.html).

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

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

8.6 Environmental specimen banking in the future

As a supporting and complementary activity in synergy with environmental monitoring, there still remain ample room for the technological development in Environmental Specimen Banking. While homogenization process is indispensable to reduce sample amount for archiving, it destroys precise sample integrity, particularly in the case of biological samples. Some chemicals, for example, may be accumulated in particular organ in higher levels and may show specific toxicity against the organ, including induction of specific proteins as exposure and / or effect markers (biomarkers). Or chemicals may cause specific morphological changes in particular organ, such as malformation of sex organ (imposex or intersex). Such specific effects may be diluted / disappeared in well-homogenized samples. Homogenization process may also change chemical integrities of the tissues / cells by destroying their microstructure and releasing various enzymes originally encapsulated within specific cell organelles. Furthermore, freezing process itself will damage microscale structure of cells / organelles by the development of micro ice-crystals /ice-needles. Once the frozen samples are thawed for the analysis, such enzymes will be released from damaged organelles and will start decomposing chemicals. Recent development of freezing process in commercial sector can reduce such a damage by preventing growth of ice-crystals / ice-needles within tissues by the use of, for example, microwave field. Cryo-preservation of a whole organism without homogenization will be developed further in future.

Long term and systematic archiving of samples representing air / water environment will be another challenge. As explained previously, some type of adsorbents, set on either passive or active sampler, are usually applied for the monitoring of pollutants in these media, and archiving part of such adsorbents or their extracts seem to be suitable for the purpose. The sampling process itself, however, may change compositions or chemical forms of pollutants in the atmosphere / water. It should be kept in mind that any sampler / adsorbent has been developed to trap particular type(s) of chemicals and that other chemicals may not be efficiently trapped; i.e., chemicals on the adsorbents may not be representative of chemicals present in the environment. In addition, chemical reactions, particularly photo-oxidation processes, may play important role to determine the fate of chemicals in the environment, but the involved chemical species tend to be quite unstable and difficult to trap in adsorbents. Further development of our understanding of the chemical processes in the environment and identification of suitable “surrogates” for the key reactions may improve the sampling strategy and archiving activity in future.

It is also important to identify major factors affecting the levels of pollutants in each media and obtain and keep relevant information together with the samples. Human levels of pollutants, for example, may change according to the change of exposure route / processes. If the major sources of proteins change from fish to beef, or from local to imported foods, in accordance with the economic development, for example, some of the POPs levels in human samples may also change accordingly. Or climate change may affect global circulation of some chemicals, and thus may affect their atmospheric levels in particular site. Even their levels in wildlife may change according to the climate change. It is now recognized that major fish species in the lower trophic levels in marine environment show decadal-scale changes due to climate change, a so-called "regime shift" (Kawasaki 1983; Chavez 2004), and pollutant levels in higher trophic level organisms, including human beings, might change accordingly in spite of no significant difference in their trophic level as shown by the stable nitrogen isotope analysis. We therefore need a deeper understanding of the environmental processes related to the levels of pollutants in target environmental / human matrices, and should collect and keep detailed additional information relevant for the proper analysis and understanding of monitoring data in addition to the archived samples themselves.

Proper understanding and recognition of the pollution status of the environment is essential and prerequisite to support decision-making processes for establishing appropriate chemical management system, including the Stockholm Convention. Environmental monitoring plays a key role to understand and recognize the pollution status by POPs, to prioritize political action, and to conduct effectiveness evaluation of the Convention. Together with the deeper understanding of key processes in the environment, Environmental Specimen Banking is expected to support the monitoring and hens the Stockholm Convention more efficiently in the future. It is important to enhancing and helping specimen banks to come about and perdure, and also to develop good international cooperation on technical issues and recommended agreed solutions. GMP could help in both.

ANNEX 1 TO THE GUIDANCE

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

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

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

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

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

Sampling

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

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

General sampling procedures

General sampling procedures include:

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

Infrastructure and set-up

With respect to sampling indispensable requirements include:

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

Standard operating procedure (SOP)

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

- The objective of the sampling exercise, including sampling protocols and specifications;
- Sample size in accordance with the analytical requirements and limitations in order to meet regulations or other objectives as given in the study;
- Description and geographic location of the sampling sites, preferentially with GPS coordinates;
- Guidelines for representative samples;

- Criteria for composite samples, e.g., number of sub-samples, homogenization;
- Description of field blank procedures;
- Date, time of the sample taking;
- Conditions during sampling;
- Time intervals between sampling exercises;
- Specifications for the sampling equipment, including the operating, maintenance, and cleaning procedures (glassware can be cleaned by heating the glass to 300 °C over night);
- Identity of the person(s) who has taken the sample;
- Full description of sample characteristics;
- Labeling (sample numbers should be assigned in the protocol and prepared labels taken into the field);
- Labeling of samples (in the field) and sample registration for further follow-up;
- Indication of expected level of POP concentration in the sample;
- Any additional observation that may assist in the interpretation of the results;
- Quality assurance procedures to prevent cross-contamination;
- The SOP should also contain a section with details on personal protective equipment that must be worn and listing of other safety concerns as appropriate.

Sub-contracting a sampling laboratory

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

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

Transport and storage

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

- Transport and storage conditions for each sample matrix including adequate facilities and infrastructure to be provided, *e.g.*, freezers;
- Preservation of integrity of samples during transport (temperature, light, etc.);
- Provisions for adequate storage, including:
    - Registry of the performance of refrigerators and freezers, e.g., registration and control of temperature;
    - Availability of automatic power-supply equipment in case of power cuts;
    - There may be limits in storage times, temperature and other conditions;

- Preservation of individual samples for their re-analysis (counter-sample);
- Pre-analytical treatment of the sample: statistical criteria to obtain sub-samples and composite samples (pools) that are representative; homogenization of solids and tissue.

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

Analysis

Key steps to be considered are:

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

Set-up and infrastructure

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

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

Extraction

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

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

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

Clean-up

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

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

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

Separation

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

- In general, an appropriate stationary phase has to be selected and enough peak separation must be achieved to allow accurate quantification (general numeric criteria cannot be given, but the use of

capillary columns with lengths of 30-60 m, internal diameters of 0.15-0.25 mm, a film thickness of 0.1-0.3 µm and helium or hydrogen as a carrier gas should ensure sufficient resolution) (note: hydrogen cannot be used together with MS detection);

- Separation of critical pairs of compounds has to be verified, e.g., pairs of PCB 28 and 31, 118 and 149; in dioxin analysis separation of PCDD/PCDF from polychlorinated diphenyl ethers (PCDE) should be checked;
- Helium, compared to nitrogen, gives a better choice to achieve the desired separation of pesticide POPs and PCB. The best carrier gas to achieve the required separation is hydrogen but it has some safety risk. If all the precautions and safety procedures are in place a hydrogen generator may be considered;
- Sample clean-up procedures should be efficient to prevent contamination of the detector;
- For PCB analysis and ECD detection, a minimum of two internal standards - one eluting at the beginning and one at the end of the chromatogram – should be used. It is recommended to also use one PCB congener that elutes in the middle of the chromatogram. Thus, the following three congeners are recommended: PCB #112, #155, and #198. These three congeners are quite stable and typically not found in commercial PCB mixtures. Note: decachlorobiphenyl (PCB #209) is not recommended because it tends to precipitate easily in standard solutions and due to long retention times, the peaks tend to be broad and have tailings. PCB #209 has also been identified in environmental samples and could not be quantified if this congener is selected as an internal standard;
- Adequate handling and preservation of all standards and reference materials.

Injection:

It is important to:

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

Identification

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

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

For HRGC-ECD combinations, the following specific recommendations are given: Retention time ± 0.2 min.

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

- Positive identification should be done on isotopic ratios within 20 % of theoretical value;
- For positive identification with MS detection, the retention time of the labelled internal standard to the native compound should be within 3 seconds;
- The use of MS libraries is useful (if full scan).

Quantification

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

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

Calibration:

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

Reporting

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

- Date, name of the sample and description, method used, the name of staff that has performed analysis, and signature of person in charge of the POPs laboratory;
- Only SI units (International System) should be used and should be verified before clearing the report;

- Clear references to the basis for the concentration must be given, *e.g.*, fresh weight, lipid weight, or volume;
- Data below the LOQ but above the LOD should be reported as "LOD-LOQ", data below LOD as "<LOD";
- Recovery efficiency should be reported;
- Measured or estimated information on the uncertainty in the results should be made available;
- Reporting values should not be corrected for percentage of recovery;
- It should be demonstrated that the blank is 10-times lower than the value that is reported. Reporting values should not be corrected by laboratory blanks (Note: There may be high fluctuations for laboratories' blanks, *e.g.*, for PCB 118). Handling of all blanks needs written documentation; in the case of high laboratory blanks; handling of such cases and justification should be clearly indicated in the SOP.

Definitions

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

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

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

There are two methods available to provide information on uncertainty:

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

Further important issues to consider:

Maintenance of equipment

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

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

Training of laboratory staff

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

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

The training requirements. Two levels of training exist:

- Training of people to follow the analytical procedures and to report the results;

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

Housing

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

- Proper environmental conditions (humidity is a most critical factor) for instrumental analysis but also for sample preparation;
- Minimization of vibration (most important for HRMS instruments);
- Temperature control for helium carrier gas used with ECD;
- At certain locations where the incoming air has to be cleaned. Ideally this would involve a well ventilated lab with air pre-filtered through HEPA (HEPA Corporation) and carbon filters. The analysis of blank samples will disclose background interferences, and to identify the influence from the laboratory environment, a small volume of a solvent left in an open Petri dish for a couple of days will catch the compounds in the atmosphere;
- Occupational Health Safety venting;
- Environmentally sound/safe disposal of laboratory wastes and highly contaminated samples must be guaranteed.

References

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

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

ANNEX 2 TO THE GUIDANCE

Part I Air Monitoring Sites

Table 1 – Global POP air monitoring network contacts

Name		Contact	Institution	Email
Australian POPs Network		Sara Broomhall	Department of the Environment and Energy (Australia)	sara.broomhall@environment.gov.au
Chinese POPs Network		Minghui Zheng	Chinese Academy of Sciences	zhengmh@rcees.ac.cn
East Asian POPs Network		Yasuyuki Shibata	National Institute for Environmental Studies (Japan)	yshibata@nies.go.jp
Spanish POPs Network		Ramon Guardans	National Reference Centre on POPs (Spain)	ramon.guardans@cnrcop.es
EMEP	European Monitoring and Evaluation Program	Pernilla Bohlin-Nizzetto	Norwegian Institute for Air Research	pernilla.bohlin.nizzetto@nilu.no
GAPS	Global Atmospheric Passive Sampling Network	Tom Harner	Environment and Climate Change Canada	tom.harner@canada.ca
GLB	Monitoring & Surveillance in the Great Lakes Basin	Hayley Hung	Environment and Climate Change Canada	hayley.hung@canada.ca
IADN	Integrated Atmospheric Deposition Network	Ron Hites	Indiana University (United States)	hitesr@indiana.edu
LAPAN	Latin America Passive Air Network	Gilberto Fillmann	Universidade Federal do Rio Grande (Brazil)	gfillmann@gmail.com
MONET	Monitoring Network	Jana Klánová	RECETOX, Masaryk University (Czech Republic)	klanova@recetox.muni.cz
NCP	Northern Contaminants Program	Hayley Hung	Environment and Climate Change Canada	hayley.hung@canada.ca
TOMPS	Toxic Organic Micro Pollutants	Andrew Sweetman	Lancaster University (United Kingdom)	a.sweetman@lancaster.ac.uk

Table 2 – Current operational air monitoring sites [2018]

Site details								Sampling details					
Network	**Country**	**Name**	**Network ID**	**Background Type**	**Latitude**	**Longitude**	**Elevation**	**Sampler**	**Type**	**Volume**	**Duration**	**Frequency**	**Since**
AFRICA													
GAPS	Egypt	Cairo	-	-	30.014056	31.486028	-	Passive	PUF	-	3 months	3 months	2018
GAPS	Kenya	Mt. Kenya	AF07	Remote	-0.062200	37.297199	3678	Passive	PUF	-	3 months	3 months	2009
GAPS	Kenya	Nairobi	-	-	-1.292066	36.821946	-	Passive	PUF	-	3 months	3 months	2018
GAPS	Nigeria	Lagos	-	-	6.524379	3.379206	-	Passive	PUF	-	3 months	3 months	2018
GAPS	Nigeria	Yaba, Lagos	AF10	-	6.500501	3.366604	8	Passive	PUF	-	3 months	3 months	2016
GAPS	South Africa	Cape Point	AF12	-	-34.350000	18.483000	-	Passive	PUF	-	3 months	3 months	2018
GAPS	South Africa	De Aar	AF04	Rural	-30.665003	23.993001	1287	Passive	PUF	-	3 months	3 months	2004
MONET	Ghana	Ghana A	3193	-	8.146740	-1.154304	-	Active	PUF	-	1 week	1 week	2014
MONET	Kenya	Chiromo Campus (Nairobi)	3179	-	-1.271917	36.804000	-	Active	PUF	-	1 week	1 week	2014
MONET	Congo	Brazzaville	183	Urban	-4.281278	15.243640	298	Passive	PUF	-	3 months	3 months	2008
MONET	Ethiopia	Asela	198	Urban	7.950000	39.116670	2327	Passive	PUF	-	3 months	3 months	2008
MONET	Ghana	Abetefi	780	-	6.683330	-0.750000	594	Passive	PUF	-	3 months	3 months	2010
MONET	Kenya	Mt. Kenya	221	Remote	-0.030000	37.220000	3678	Passive	PUF	-	3 months	3 months	2008
MONET	Mauritius	Reduit	246	Suburban	-20.233200	57.498490	310	Passive	PUF	-	3 months	3 months	2008
MONET	Morocco	Morocco Observatory	4026	-	33.925000	-6.758000	-	Passive	PUF	-	3 months	3 months	2014
MONET	Nigeria	Sheda	267	Suburban	8.881000	7.062167	229	Passive	PUF	-	3 months	3 months	2008
EAST ASIA & PACIFIC													
China	China	Changdao	B2	Remote	37.989720	120.695600	-	Active	PUF	~300 m³/d	3+ days	1 year	2008
China	China	Chengde	B10	Remote	41.119720	116.494400	-	Active	PUF	~300 m³/d	3+ days	1 year	2008
China	China	Chongqing	U1	Urban	29.645560	106.561900	-	Active	PUF	~300 m³/d	3+ days	1 year	2012
China	China	Daxinganling	B8	Remote	50.880830	121.249700	-	Active	PUF	~300 m³/d	3+ days	1 year	2008
China	China	Hong Kong	-	Urban	22.267200	114.187900	-	Active	-	-	-	-	1998
China	China	Lasa	B5	Remote	29.353610	90.742220	-	Active	PUF	~300 m³/d	3+ days	1 year	2008
China	China	Lijiang	B6	Remote	26.881670	100.250000	-	Active	PUF	~300 m³/d	3+ days	1 year	2008
China	China	Luan	B4	Remote	31.551390	116.160000	-	Active	PUF	~300 m³/d	3+ days	1 year	2008
China	China	Nanjing	U3	Urban	32.043060	118.745600	-	Active	PUF	~300 m³/d	3+ days	1 year	2012
China	China	Qinghaihu	B11	Remote	36.583890	100.493300	-	Active	PUF	~300 m³/d	3+ days	1 year	2008
China	China	Qingyuan	B1	Remote	41.852220	124.937800	-	Active	PUF	~300 m³/d	3+ days	1 year	2008
China	China	Rizhao	R1	Rural	35.693610	119.314400	-	Active	PUF	~300 m³/d	3+ days	1 year	2012

Site details								Sampling details					
Network	**Country**	**Name**	**Network ID**	**Background Type**	**Latitude**	**Longitude**	**Elevation**	**Sampler**	**Type**	**Volume**	**Duration**	**Frequency**	**Since**
China	China	Shennongjia	B7	Remote	31.457220	110.271100	-	Active	PUF	~300 m³/d	3+ days	1 year	2011
China	China	Wuhan	U2	Urban	29.972220	114.160000	-	Active	PUF	~300 m³/d	3+ days	1 year	2012
China	China	Wulong	B9	Remote	29.510830	107.746400	-	Active	PUF	~300 m³/d	3+ days	1 year	2008
China	China	Wuyishan	B3	Remote	27.586670	117.730000	-	Active	PUF	~300 m³/d	3+ days	1 year	2011
China	China	Yangshuo	R2	Rural	24.792500	110.510000	-	Active	PUF	~300 m³/d	3+ days	1 year	2012
East Asia	Cambodia	Sihanoukville	-	-	10.633333	103.516667	130	Active	PUF	-	-	-	2009
East Asia	Indonesia	Kototabang	-	Remote	-0.202300	100.317900	864	Active	PUF	-	-	-	2012
East Asia	Japan	Hedo / Cape Hedo, Okinawa	-	Remote	26.870000	128.260000	37	Active	PUF	~1000 m³/d	3 days	1 month	2009
East Asia	Laos	Na Long Koun Village	-	Remote	18.295800	102.269400	174	Active	PUF	-	-	-	2011
East Asia	Malaysia	Batu Embun	-	Remote	3.971000	102.347800	77	Active	PUF	-	-	-	2009
East Asia	Mongolia	Terelj	-	High altitude	47.983300	107.450000	1560	Active	PUF	-	-	-	2013
East Asia	Philippines	Sto Tomas Mountain	-	High altitude	16.358100	120.557600	2040	Active	PUF	-	-	-	2011
East Asia	South Korea	Cheju / Jeju Island	-	Remote	33.170000	126.100000	24	Active	PUF	~1000 m³/d	3 days	1 month	2009
East Asia	Vietnam	Tam Dao	-	Remote	21.460000	105.650000	934	Active	PUF	~1000 m³/d	3 days	3 months	2009
GAPS	China	Beijing	-	-	39.904200	116.407396	-	Passive	PUF	-	3 months	3 months	2018
GAPS	India	Kolkata	-	-	22.572646	88.363895	-	Passive	PUF	-	3 months	3 months	2018
GAPS	India	New Delhi	-	-	28.588493	77.227582	-	Passive	PUF	-	3 months	3 months	2018
GAPS	Indonesia	Bukit Kototabang	AS13	-	0.200000	100.320000	864	Passive	PUF	-	3 months	3 months	2004
GAPS	Japan	Tokyo	-	-	35.689488	139.691706	-	Passive	PUF	-	3 months	3 months	2018
GAPS	Kuwait	Abdaly	AS21	-	29.978833	47.706333	52	Passive	PUF	-	3 months	3 months	2007
GAPS	Malaysia	Danum Valley	AS12	-	4.981390	117.843610	426	Passive	PUF	-	3 months	3 months	2004
GAPS	Maldives	Hanimaadhoo	AS28	-	6.776300	73.183300	-	Passive	PUF	-	3 months	3 months	2018
GAPS	Philippines	Manila	AS11	Urban	14.651944	121.068889	74	Passive	PUF	-	3 months	3 months	2005
GAPS	South Korea	Gosan, Jeju Island	AS19	-	33.293611	126.162778	49	Passive	PUF	-	3 months	3 months	2007
GAPS	Sri Lanka	Wilgamuwa	AS27	-	7.521880	80.952994	-	Passive	PUF	-	3 months	3 months	2018
GAPS	Thailand	Bangkok	-	-	13.723528	100.521611	-	Passive	PUF	-	3 months	3 months	2018
AUSTRALIA, CANADA, NEW ZEALAND & UNITED STATES													
Australia	Australia	Aspendale, VIC	-	-	-38.024167	145.102500	8	Active	PUF	-	-	-	2010
Australia	Australia	Cape Grim, TAS	CPG	-	-40.682778	144.690000	94	Active	PUF	-	-	-	2010
Australia	Australia	Darwin, NT	DAR	-	-12.412500	130.920278	30	Active	PUF	-	-	-	2010
Australia	Australia	Alice Springs, NT	ALI	-	-23.795100	133.889000	547	Passive	XAD	-	1 year	1 year	2013
Australia	Australia	Aspendale, VIC	-	-	-38.024261	145.102581	8	Passive	XAD	-	1 year	1 year	2013

Site details								Sampling details					
Network	Country	Name	Network ID	Background Type	Latitude	Longitude	Elevation	Sampler	Type	Volume	Duration	Frequency	Since
Australia	Australia	Barossa, SA	BAR	-	-34.468775	139.008506	284	Passive	XAD	-	1 year	1 year	2011
Australia	Australia	Brisbane, QLD	BRI	-	-27.498964	153.036683	20	Passive	XAD	-	1 year	1 year	2010
Australia	Australia	Burdekin, QLD	BUR	-	-19.570755	147.323655	11	Passive	XAD	-	1 year	1 year	2011
Australia	Australia	Cape Grim, TAS	CPG	-	-40.682667	144.689827	85	Passive	XAD	-	1 year	1 year	2011
Australia	Australia	Condamine - Brookstead, QLD	CON	-	-27.785975	151.427762	381	Passive	XAD	-	1 year	1 year	2011
Australia	Australia	Condamine - Dalby, QLD	CON	-	-27.149695	151.273949	348	Passive	XAD	-	1 year	1 year	2011
Australia	Australia	Condamine - Toowoomba, QLD	CON	-	-27.534962	151.929945	647	Passive	XAD	-	1 year	1 year	2011
Australia	Australia	Condamine - Warwick, QLD	CON	-	-28.206043	152.100084	480	Passive	XAD	-	1 year	1 year	2011
Australia	Australia	Darwin, NT	DAR	-	-12.412600	130.920200	43	Passive	XAD	-	1 year	1 year	2011
Australia	Australia	Dunk Island, QLD	DUN	-	-17.936431	146.137049	15	Passive	XAD	-	1 year	1 year	2011
Australia	Australia	Giles, WA	GIL	-	-25.033818	128.302543	599	Passive	XAD	-	1 year	1 year	2010
Australia	Australia	Gladstone, QLD	GLA	-	-23.857391	151.269755	12	Passive	XAD	-	1 year	1 year	2010
Australia	Australia	Gunn Point, NT	GPO	-	-12.249128	131.044433	28	Passive	XAD	-	1 year	1 year	2014
Australia	Australia	Gunnedah, NSW	GUN	-	-31.026064	150.273329	287	Passive	XAD	-	1 year	1 year	2011
Australia	Australia	Halls Creek, WA	HAL	-	-18.229200	127.663600	425	Passive	XAD	-	1 year	1 year	2013
Australia	Australia	Heron Island, QLD	HER	-	-23.443058	151.914130	8	Passive	XAD	-	1 year	1 year	2012
Australia	Australia	Idalia National Park, QLD	IDA	-	-24.891205	144.684637	379	Passive	XAD	-	1 year	1 year	2011
Australia	Australia	Kakadu - East Alligator, NT	KEA	-	-12.493074	132.982979	128	Passive	XAD	-	1 year	1 year	2011
Australia	Australia	Kakadu - Mary River, NT	KMR	-	-13.778912	131.870613	190	Passive	XAD	-	1 year	1 year	2011
Australia	Australia	Kalbarri - National Park, WA	KLB	-	-27.810367	114.464558	206	Passive	XAD	-	1 year	1 year	2011
Australia	Australia	Kalbarri - Park HQ, WA	KLB	-	-27.695068	114.182195	19	Passive	XAD	-	1 year	1 year	2011
Australia	Australia	Kalgoorlie, WA	KLG	-	-30.750840	121.463050	367	Passive	XAD	-	1 year	1 year	2010
Australia	Australia	Karratha - Airport, WA	KAR	-	-20.708558	116.774347	8	Passive	XAD	-	1 year	1 year	2011
Australia	Australia	Karratha - Office/Town, WA	KAR	-	-20.737036	116.845720	17	Passive	XAD	-	1 year	1 year	2011
Australia	Australia	Kununurra - Middle Springs, WA	KUN	-	-15.633765	128.669735	61	Passive	XAD	-	1 year	1 year	2010
Australia	Australia	Kununurra - Town Centre, WA	KUN	-	-15.653384	128.706960	37	Passive	XAD	-	1 year	1 year	2010
Australia	Australia	Lockyer Valley - Gatton, QLD	LKV	-	-27.544028	152.330053	94	Passive	XAD	-	1 year	1 year	2010
Australia	Australia	Mackay - Cannonvale, QLD	CAN	-	-20.279770	148.692450	24	Passive	XAD	-	1 year	1 year	2016
Australia	Australia	Mackay - Eungella, QLD	EUN	-	-21.145467	148.499132	772	Passive	XAD	-	1 year	1 year	2011
Australia	Australia	McLaren Vale, SA	MCV	-	-35.177022	138.543055	139	Passive	XAD	-	1 year	1 year	2011
Australia	Australia	Melbourne, VIC	MEL	-	-37.808717	144.965045	44	Passive	XAD	-	1 year	1 year	2011
Australia	Australia	Merredin, WA	MER	-	-31.481244	118.276466	322	Passive	XAD	-	1 year	1 year	2011

Site details								Sampling details					
Network	**Country**	**Name**	**Network ID**	**Background Type**	**Latitude**	**Longitude**	**Elevation**	**Sampler**	**Type**	**Volume**	**Duration**	**Frequency**	**Since**
Australia	Australia	Mildura, VIC	MIL	-	-34.219114	142.191915	59	Passive	XAD	-	1 year	1 year	2010
Australia	Australia	Mullewa, WA	MUL	-	-28.540069	115.512733	277	Passive	XAD	-	1 year	1 year	2011
Australia	Australia	Narangba, QLD	NAR	-	-27.199004	153.001643	19	Passive	XAD	-	1 year	1 year	2011
Australia	Australia	New Town - Hobart, TAS	NEW	-	-42.861519	147.304045	50	Passive	XAD	-	1 year	1 year	2011
Australia	Australia	North Haven Adelaide, SA	NHA	-	-34.791293	138.497778	6	Passive	XAD	-	1 year	1 year	2017
Australia	Australia	One Tree Island, QLD	OTI	-	-23.506642	152.091731	2	Passive	XAD	-	1 year	1 year	2011
Australia	Australia	Orpheus Island, QLD	ORP	-	-18.615187	146.488255	10	Passive	XAD	-	1 year	1 year	2013
Australia	Australia	Perth - Duncraig, WA	PER	-	-31.833087	115.783525	18	Passive	XAD	-	1 year	1 year	2010
Australia	Australia	Phillip Island, VIC	PHI	-	-38.473552	145.236614	38	Passive	XAD	-	1 year	1 year	2011
Australia	Australia	Snowy Mountains, NSW	SNM	-	-36.414981	148.622075	927	Passive	XAD	-	1 year	1 year	2011
Australia	Australia	Stradbroke Island, QLD	NSI	-	-27.436486	153.545621	28	Passive	XAD	-	1 year	1 year	2010
Australia	Australia	Sydney 1 - Rozelle, NSW	ROZ	-	-33.864048	151.164026	27	Passive	XAD	-	1 year	1 year	2010
Australia	Australia	Sydney 2 - Homebush, NSW	HBB	-	-33.823266	151.083267	1	Passive	XAD	-	1 year	1 year	2010
Australia	Australia	Tatura, VIC	TAT	-	-36.439960	145.267308	114	Passive	XAD	-	1 year	1 year	2011
Australia	Australia	Tully, QLD	TUL	-	-17.746389	146.050555	13	Passive	XAD	-	1 year	1 year	2011
Australia	Australia	Uluru, NT	ULU	-	-25.370556	130.997778	533	Passive	XAD	-	1 year	1 year	2011
GAPS	Australia	Cape Grim	WE23	Remote	-40.683619	144.700932	71	Passive	PUF	-	3 months	3 months	2004
GAPS	Australia	Darwin	WE22	Rural	-12.370667	130.864500	8	Passive	PUF	-	3 months	3 months	2004
GAPS	Australia	Sydney	-	-	-33.868820	151.209296	-	Passive	PUF	-	3 months	3 months	2018
GAPS	Canada	Alert, NU	WE01	Polar	82.450133	-63.503967	0	Passive	PUF	-	3 months	3 months	2004
GAPS	Canada	Bratts Lake, SK	WE05	Remote	50.200833	-104.710278	595	Passive	PUF	-	3 months	3 months	2004
GAPS	Canada	Coral Harbour, NU	WE42	-	64.133333	-83.166667	9	Passive	PUF	-	3 months	3 months	2004
GAPS	Canada	Downsview, ON	WE09	Urban	43.781111	-79.468333	184	Passive	PUF	-	3 months	3 months	2004
GAPS	Canada	Egbert / CARE Station, ON	WE47	Rural	44.233000	-79.783000	242	Passive	PUF	-	3 months	3 months	2013
GAPS	Canada	Fraserdale, ON	WE32	-	49.883333	-81.566667	166	Passive	PUF	-	3 months	3 months	2007
GAPS	Canada	Little Fox Lake, YT	WE25	Polar	61.349996	-135.633337	1072	Passive	PUF	-	3 months	3 months	2006
GAPS	Canada	Longwoods, ON	WE45	Rural	42.883333	-81.480556	237	Passive	PUF	-	3 months	3 months	2013
GAPS	Canada	Mount Revelstoke, BC	WE43	-	51.070030	-118.108719	1917	Passive	SIP	-	1 year	1 year	2009
GAPS	Canada	Sable Island, NS	WE34	-	43.560000	-60.010000	4	Passive	PUF	-	3 months	3 months	2007
GAPS	Canada	Toronto	-	-	43.658952	-79.395595	-	Passive	PUF	-	3 months	3 months	2018
GAPS	Canada	Ucluelet, BC	WE33	-	48.933333	-125.516667	14	Passive	PUF	-	3 months	3 months	2007
GAPS	Canada	Warsaw Caves, ON	WE46	Rural	44.463889	-78.130556	226	Passive	PUF	-	3 months	3 months	2013

Site details								Sampling details					
Network	**Country**	**Name**	**Network ID**	**Background Type**	**Latitude**	**Longitude**	**Elevation**	**Sampler**	**Type**	**Volume**	**Duration**	**Frequency**	**Since**
GAPS	Canada	Whistler, BC	WE06	-	50.058333	-122.956944	2180	Passive	PUF	-	3 months	3 months	2004
GAPS	New Zealand	Temple Basin, Arthurs Pass	WE39	-	-42.908889	171.574722	1345	Passive	PUF	-	3 months	3 months	2009
GAPS	United States	Barrow, AK	WE02	Polar	71.320000	-156.600000	5	Passive	PUF	-	3 months	3 months	2004
GAPS	United States	Dyea, AK	WE26	Polar	59.520396	-135.350135	23	Passive	PUF	-	3 months	3 months	2006
GAPS	United States	Groton, CT	WE40	-	41.316710	-72.066698	4	Passive	PUF	-	3 months	3 months	2009
GAPS	United States	Mauna Loa Obs, Hilo, HI	WE37	-	19.540000	-155.580000	3319	Passive	PUF	-	3 months	3 months	2007
GAPS	United States	New York City	-	-	40.712775	-74.005973	-	Passive	PUF	-	3 months	3 months	2018
GAPS	United States	Point Reyes, CA	WE35	-	38.041550	-122.794370	37	Passive	PUF	-	3 months	3 months	2007
GAPS	United States	St. Lawrence Island, AK	WE03	Polar	63.696791	-170.498002	4	Passive	PUF	-	3 months	3 months	2005
GAPS	United States	Tula, American Samoa	WE38	-	-14.240000	-170.570000	42	Passive	PUF	-	3 months	3 months	2007
GLB	Canada	Georgian Bay Island National Park	-	-	44.847700	-79.864300	-	Passive	PUF	-	3 months	3 months	2013
GLB	Canada	Gros Cap	-	-	46.541600	-84.591800	-	Passive	PUF	-	3 months	3 months	2013
GLB	Canada	Manitoulin Island/Evansville	-	-	45.819300	-82.651500	-	Passive	PUF	-	3 months	3 months	2013
GLB	Canada	Point Pelee	-	-	41.966700	-82.532800	-	Passive	PUF	-	3 months	3 months	2013
GLB	Canada	Georgian Bay Island National Park	-	-	44.847700	-79.864300	-	Passive	XAD	-	1 year	1 year	2013
GLB	Canada	Gros Cap	-	-	46.541600	-84.591800	-	Passive	XAD	-	1 year	1 year	2013
GLB	Canada	Manitoulin Island/Evansville	-	-	45.819300	-82.651500	-	Passive	XAD	-	1 year	1 year	2013
GLB	Canada	Point Pelee	-	-	41.966700	-82.532800	-	Passive	XAD	-	1 year	1 year	2013
GLB/IADN	Canada	Point Petre	-	Rural	43.833300	-77.150000	78	Active	PUF	~350 m³/d	24 hr	36 days	1992
IADN	United States	Chicago	-	Urban	41.834400	-87.624720	199	Active	XAD	~815 m³/d	24 hr	12 days	1996
IADN	United States	Cleveland	-	Urban	41.492100	-81.678500	204	Active	XAD	~815 m³/d	24 hr	12 days	2003
IADN	United States	Eagle harbor	-	Remote	47.459700	-88.149200	185	Active	XAD	~815 m³/d	24 hr	12 days	1990
IADN	United States	Sleeping Bear Dunes	-	Remote	44.761100	-86.058610	241	Active	XAD	~815 m³/d	24 hr	12 days	1991
IADN	United States	Sturgeon Point	-	Rural	42.692800	-79.038900	54	Active	XAD	~815 m³/d	24 hr	12 days	1991
NCP	Canada	Alert, NU	-	-	82.450133	-63.503967	-	Active	PUF	-	-	-	1992
NCP	Canada	Cambridge Bay, NU	-	-	69.133333	-105.050000	-	Passive	PUF	-	3 months	3 months	2017
NCP	Canada	Fort Resolution, NT	-	-	61.166667	-113.750000	-	Passive	PUF	-	3 months	3 months	2015
NCP	Canada	Inuvik, NT	-	-	68.350000	-133.716667	-	Passive	PUF	-	3 months	3 months	2015
NCP	Canada	Iqaluit, NU	-	-	63.740972	-68.465833	-	Passive	PUF	-	3 months	3 months	2014
NCP	Canada	Kuujjuaq, QC	-	-	58.250000	-68.350000	-	Passive	PUF	-	3 months	3 months	2015
NCP	Canada	Nain, NL	-	-	56.525278	-61.724722	-	Passive	PUF	-	3 months	3 months	2015
NCP	Canada	Northwest River, NL	-	-	53.560556	-60.137222	-	Passive	PUF	-	3 months	3 months	2017

Site details								Sampling details					
Network	**Country**	**Name**	**Network ID**	**Background Type**	**Latitude**	**Longitude**	**Elevation**	**Sampler**	**Type**	**Volume**	**Duration**	**Frequency**	**Since**
NCP	Canada	Cambridge Bay, NU	-	-	69.133333	-105.050000	-	Passive	XAD	-	1 year	1 year	2017
NCP	Canada	Fort Resolution, NT	-	-	61.166667	-113.750000	-	Passive	XAD	-	1 year	1 year	2015
NCP	Canada	Inuvik, NT	-	-	68.350000	-133.716667	-	Passive	XAD	-	1 year	1 year	2015
NCP	Canada	Iqaluit, NU	-	-	63.740972	-68.465833	-	Passive	XAD	-	1 year	1 year	2014
NCP	Canada	Kuujjuaq, QC	-	-	58.250000	-68.350000	-	Passive	XAD	-	1 year	1 year	2015
NCP	Canada	Nain, NL	-	-	56.525278	-61.724722	-	Passive	XAD	-	1 year	1 year	2015
NCP	Canada	Northwest River, NL	-	-	53.560556	-60.137222	-	Passive	XAD	-	1 year	1 year	2017
EUROPE & WEST ASIA													
EMEP	Czech Republic	Košetice	CZ0003R	Rural	49.573450	15.080410	534	Active	PUF	~700 m³/d	24 h	1 week	2005
EMEP	Finland	Pallas / Matorova	FI0036R	Polar	68.000480	24.245660	340	Active	-	Hi. Vol.	-	1 week	1996
EMEP	Norway	Andoya	NO0090R	Polar	69.278330	16.011670	380	Active	PUF	~500 m³/d	-	1 week	2009
EMEP	Norway	Birkenes II	NO0002R	Remote	58.388330	8.251940	190	Active	PUF	~500 m³/d	-	1 week	2009
EMEP	Norway	Ny-Ålesund / Spitsbergen / Zeppelinfjell	NO0042G	Polar	78.880000	11.883330	474	Active	PUF	~500 m³/d	48 h	1 week	1993
EMEP	Sweden	Aspvreten	SE0012R	Remote	58.805800	17.388400	20	Active	-	Hi. Vol.	-	1 week	1995
EMEP	Sweden	Rao	SE0014R	Remote	57.393670	11.914170	5	Active	-	Hi. Vol.	-	1 week	2002
GAPS	Czech Republic	Košetice	EE03	Rural	49.583566	15.083725	534	Passive	PUF	-	3 months	3 months	2004
GAPS	Finland	Pallas / Matorova	WE30	Polar	68.000000	24.240000	324	Passive	PUF	-	3 months	3 months	2005
GAPS	France	Paris	WE17	Urban	48.863950	2.358269	35	Passive	PUF	-	3 months	3 months	2005
GAPS	Iceland	Storhofdi	WE14	Remote	63.400000	-20.283000	82	Passive	PUF	-	3 months	3 months	2004
GAPS	Ireland	Malin Head	WE16	Rural	55.371672	-7.338988	18	Passive	PUF	-	3 months	3 months	2004
GAPS	Norway	Ny-Ålesund / Spitsbergen / Zeppelinfjell	WE13	Polar	78.907250	11.886667	475	Passive	PUF	-	3 months	3 months	2004
GAPS	Poland	Warsaw	-	-	52.221611	21.007250	-	Passive	PUF	-	3 months	3 months	2018
GAPS	Spain	Doñana National Park	WE41	-	37.053333	-6.554167	35	Passive	PUF	-	3 months	3 months	2009
GAPS	Spain	Izana	WE44	-	28.308983	-16.499384	2367	Passive	PUF	-	3 months	3 months	2013
GAPS	Spain	Madrid	-	-	40.443194	-3.684611	-	Passive	PUF	-	3 months	3 months	2018
GAPS	Turkey	Istanbul	-	-	41.008238	28.978359	-	Passive	PUF	-	3 months	3 months	2018
GAPS	United Kingdom	London	-	-	51.507351	-0.127758	-	Passive	PUF	-	3 months	3 months	2018
MONET	Czech Republic	Košetice	17	Rural	49.573450	15.080410	584	Active	PUF	~700 m³/d	24 h	1 week	1989
MONET	Austria	Sonnblick [EMEP]	740	Remote	47.054030	12.957660	3110	Passive	PUF	-	3 months	3 months	2009
MONET	Bulgaria	Moussala [EMEP]	743	-	42.179160	23.585280	2925	Passive	PUF	-	3 months	3 months	2009
MONET	Croatia	Zagreb, Siget	203	Suburban	45.773530	15.984580	-	Passive	PUF	-	3 months	3 months	2007
MONET	Cyprus	Ayia Marina [EMEP]	744	Rural	35.038056	33.057778	532	Passive	PUF	-	3 months	3 months	2009

Site details								Sampling details					
Network	**Country**	**Name**	**Network ID**	**Background Type**	**Latitude**	**Longitude**	**Elevation**	**Sampler**	**Type**	**Volume**	**Duration**	**Frequency**	**Since**
MONET	Czech Republic	Bily Kriz, Beskydy	2	Remote	49.502610	18.538560	828	Passive	PUF	-	3 months	3 months	2006
MONET	Czech Republic	Brno, Lisen, CHMI station	695	Rural	49.213333	16.678056	344	Passive	PUF	-	3 months	3 months	2010
MONET	Czech Republic	Churanov, Sumava [EMEP]	13	Remote	49.068440	13.614880	1121	Passive	PUF	-	3 months	3 months	2006
MONET	Czech Republic	Dolni Lutyne, Vernovice	647	Rural	49.924722	18.422778	202	Passive	PUF	-	3 months	3 months	2010
MONET	Czech Republic	Jesenik, Jeseniky	15	Rural	50.242250	17.190220	625	Passive	PUF	-	3 months	3 months	2006
MONET	Czech Republic	Klet, Sumava	16	Remote	48.863890	14.284410	1060	Passive	PUF	-	3 months	3 months	2006
MONET	Czech Republic	Kosetice [EMEP]	17	Rural	49.573450	15.080410	503	Passive	PUF	-	3 months	3 months	2003
MONET	Czech Republic	Liberec, Jested	23	Remote	50.729400	14.987900	930	Passive	PUF	-	3 months	3 months	2005
MONET	Czech Republic	Mikulov, Sedlec	50	Rural	48.791750	16.724500	232	Passive	PUF	-	3 months	3 months	2006
MONET	Czech Republic	Planavy (Sitna nad Vlari-Popov, Planavy)	66	Remote	49.047760	18.007810	561	Passive	PUF	-	3 months	3 months	2004
MONET	Czech Republic	Praha, Libus, CHMI Station [EMEP]	39	Urban	50.007310	14.446200	302	Passive	PUF	-	3 months	3 months	2004
MONET	Czech Republic	Prebuz	355	Rural	50.372500	12.615278	907	Passive	PUF	-	3 months	3 months	2008
MONET	Czech Republic	Primda, Sumava	41	Rural	49.669590	12.677850	704	Passive	PUF	-	3 months	3 months	2006
MONET	Czech Republic	Rudolice (Rudolice v Horach, Krusne hory)	46	Remote	50.579790	13.419220	852	Passive	PUF	-	3 months	3 months	2006
MONET	Czech Republic	Rychory (Rychory, Krkonose)	49	Remote	50.660460	15.850060	948	Passive	PUF	-	3 months	3 months	2006
MONET	Czech Republic	Sneznik (Decinsky Sneznik, Labske piskovce)	11	Remote	50.789510	14.086840	597	Passive	PUF	-	3 months	3 months	2006
MONET	Czech Republic	Svratouch [EMEP]	62	Rural	49.735070	16.034130	735	Passive	PUF	-	3 months	3 months	2006
MONET	Estonia	Lahemaa [EMEP]	194	Remote	59.515280	25.928050	61	Passive	PUF	-	3 months	3 months	2006
MONET	Finland	Pallas [EMEP]	746	Polar	68.000480	24.245660	340	Passive	PUF	-	3 months	3 months	2009
MONET	France	Le Montfranc [EMEP]	748	Rural	45.809990	2.060000	810	Passive	PUF	-	3 months	3 months	2009
MONET	France	Peyrusse Vieille [EMEP]	749	Rural	43.630270	0.179722	175	Passive	PUF	-	3 months	3 months	2009
MONET	Hungary	K-puszta [EMEP]	753	Rural	46.967500	19.553060	-	Passive	PUF	-	3 months	3 months	2009
MONET	Iceland	Storhofdi [EMEP]	754	Remote	63.400000	-20.283330	118	Passive	PUF	-	3 months	3 months	2009
MONET	Latvia	Rucava [EMEP]	236	Rural	56.161960	21.173220	16	Passive	PUF	-	3 months	3 months	2006
MONET	Lithuania	Plateliai	232	Rural	56.010000	21.886950	150	Passive	PUF	-	3 months	3 months	2006
MONET	Malta	Giordan Lighthouse [EMEP]	760	Rural	36.073330	14.219170	167	Passive	PUF	-	3 months	3 months	2009
MONET	Netherlands	De Zilk [EMEP]	761	Rural	52.296570	4.510860	-	Passive	PUF	-	3 months	3 months	2009
MONET	Norway	Birkenes [EMEP]	762	Remote	58.383340	8.250000	190	Passive	PUF	-	3 months	3 months	2009
MONET	Norway	Karvatn [EMEP]	763	Remote	62.783330	8.883333	210	Passive	PUF	-	3 months	3 months	2009
MONET	Norway	Spitsbergen / Zeppelinfjell [EMEP]	764	Polar	78.880000	11.883330	474	Passive	PUF	-	3 months	3 months	2009
MONET	Poland	Diabla Gora [EMEP]	765	Rural	54.124870	22.038080	157	Passive	PUF	-	3 months	3 months	2009
MONET	Russia	Ufa, ERPC	767	-	54.466450	56.012330	175	Passive	PUF	-	3 months	3 months	2009

Site details								Sampling details					
Network	**Country**	**Name**	**Network ID**	**Background Type**	**Latitude**	**Longitude**	**Elevation**	**Sampler**	**Type**	**Volume**	**Duration**	**Frequency**	**Since**
MONET	Serbia	Fruska Gora	328	Remote	45.159170	19.862810	514	Passive	PUF	-	3 months	3 months	2004
MONET	Slovakia	Starina [EMEP]	312	Rural	49.042690	22.260000	345	Passive	PUF	-	3 months	3 months	2006
MONET	Slovenia	Iskrba [EMEP]	317	Rural	45.561390	14.862780	520	Passive	PUF	-	3 months	3 months	2007
MONET	Sweden	Rao [EMEP]	771	Remote	57.393670	11.914170	10	Passive	PUF	-	3 months	3 months	2009
MONET	Switzerland	Payerne [EMEP]	772	Rural	46.800000	6.933330	489	Passive	PUF	-	3 months	3 months	2009
MONET	Turkey	Camkoru	773	Rural	40.584690	32.504860	1406	Passive	PUF	-	3 months	3 months	2009
MONET	Ukraine	Zmiinyi Island [EMEP]	774	Remote	45.256110	30.201060	28	Passive	PUF	-	3 months	3 months	2009
MONET	United Kingdom	High Muffles [EMEP]	776	Rural	54.334944	-0.808550	270	Passive	PUF	-	3 months	3 months	2009
Spain	Spain	Albacete	EC08	Urban	39.000000	-1.850000	-	Passive	PUF	-	3 months	3 months	2008
Spain	Spain	Azpeitia	U1	Urban	43.181944	-2.265278	-	Passive	PUF	-	3 months	3 months	2008
Spain	Spain	Badajoz	EC07	Urban	38.883333	-7.000000	-	Passive	PUF	-	3 months	3 months	2008
Spain	Spain	Barcarrola	ES0011R	Remote	38.475833	-6.922778	393	Passive	PUF	-	3 months	3 months	2008
Spain	Spain	Barcelona	U2	Urban	41.386667	2.201111	-	Passive	PUF	-	3 months	3 months	2009
Spain	Spain	Cabo de Creus	ES0010R	Remote	42.319444	3.316944	23	Passive	PUF	-	3 months	3 months	2008
Spain	Spain	Campisabalos	ES0009R	Remote	41.281111	-3.142778	1360	Passive	PUF	-	3 months	3 months	2008
Spain	Spain	Doñana	ES0017R	Remote	37.030278	-6.331667	5	Passive	PUF	-	3 months	3 months	2008
Spain	Spain	Els Torms	ES0014R	Remote	41.400000	0.716667	470	Passive	PUF	-	3 months	3 months	2008
Spain	Spain	Huelva	U3	Urban	37.250000	-6.950000	-	Passive	PUF	-	3 months	3 months	2009
Spain	Spain	Izana	ES0018G	Remote	28.308889	-16.499167	2373	Passive	PUF	-	3 months	3 months	2011
Spain	Spain	La Coruña	U4	Urban	43.365833	-8.421389	-	Passive	PUF	-	3 months	3 months	2009
Spain	Spain	Madrid	EC05	Urban	40.450000	-3.716667	-	Passive	PUF	-	3 months	3 months	2008
Spain	Spain	Mahón	ES0006R	Remote	39.866667	4.316667	78	Passive	PUF	-	3 months	3 months	2008
Spain	Spain	Niembro	ES0008R	Remote	43.442222	-4.850278	134	Passive	PUF	-	3 months	3 months	2008
Spain	Spain	Noia	ES0005R	Remote	42.728056	-8.923611	683	Passive	PUF	-	3 months	3 months	2008
Spain	Spain	O Saviñao	ES0016R	Remote	43.231111	-7.699722	506	Passive	PUF	-	3 months	3 months	2008
Spain	Spain	Penausende	ES0013R	Remote	41.283333	-5.866667	985	Passive	PUF	-	3 months	3 months	2008
Spain	Spain	S.C. Tenerife	U5	Urban	28.472528	-16.247222	-	Passive	PUF	-	3 months	3 months	2011
Spain	Spain	San Pablo de los Montes	ES0001R	Remote	39.547778	-4.348611	917	Passive	PUF	-	3 months	3 months	2008
Spain	Spain	Valladolid	EC06	Urban	41.633333	-4.750000	-	Passive	PUF	-	3 months	3 months	2008
Spain	Spain	Víznar	ES0007R	Remote	37.233333	-3.533333	1265	Passive	PUF	-	3 months	3 months	2008
Spain	Spain	Zarra	ES0012R	Remote	39.086111	-1.101944	885	Passive	PUF	-	3 months	3 months	2008
TOMPS	United Kingdom	Auchencorth Moss	AC	Rural	55.793330	-3.244722	-	Active	PUF	~50 m^3/d	2 weeks	2 weeks	2008

Site details								Sampling details					
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TOMPS	United Kingdom	Hazelrigg	HR	Rural	54.013610	-2.773617	-	Active	PUF	~50 m³/d	2 weeks	2 weeks	2004
TOMPS	United Kingdom	High Muffles	HM	Rural	54.334940	-0.808550	-	Active	PUF	~50 m³/d	2 weeks	2 weeks	2004
TOMPS	United Kingdom	London	LON	Urban	51.495530	-0.126414	-	Active	PUF	~50 m³/d	2 weeks	2 weeks	2004
TOMPS	United Kingdom	Manchester	MAN	Urban	53.480800	-2.251980	-	Active	PUF	~50 m³/d	2 weeks	2 weeks	2004
TOMPS	United Kingdom	Weybourne	WE	Rural	52.950490	1.122017	-	Active	PUF	~50 m³/d	2 weeks	2 weeks	2009
LATIN AMERICA & CARIBBEAN													
GAPS	Argentina	Mendoza Province	GR21	Rural	-32.709223	-68.400447	596	Passive	PUF	-	3 months	3 months	2011
GAPS	Argentina	Pierre Auger Observatory	GR20	-	-35.113727	-65.599903	329	Passive	PUF	-	3 months	3 months	2011
GAPS	Argentina	Rio Gallegos	GR27	Rural	-51.647310	-69.207310	18	Passive	PUF	-	3 months	3 months	2012
GAPS	Argentina	Salta	GR26	Remote	-25.085132	-66.126223	-	Passive	PUF	-	3 months	3 months	2011
GAPS	Barbados	Ragged Point, St. Philip	GR12	-	13.165051	-59.432151	0	Passive	PUF	-	3 months	3 months	2008
GAPS	Bermuda	Tudor Hill	WE12	Rural	32.366667	-64.650000	24	Passive	PUF	-	3 months	3 months	2004
GAPS	Bolivia	Chacaltaya	GR29	-	-16.210000	-68.080000	5240	Passive	PUF	-	3 months	3 months	2015
GAPS	Brazil	Itatiaia	GR25	-	-22.385833	-44.678889	2400	Passive	PUF	-	3 months	3 months	2014
GAPS	Brazil	São José dos Ausentes	GR24	Remote	-28.594170	-49.818590	1270	Passive	PUF	-	3 months	3 months	2012
GAPS	Brazil	São Luis do Maranhão	GR23	Urban	-2.353600	-44.123900	10	Passive	PUF	-	3 months	3 months	2012
GAPS	Brazil	Sao Paulo	-	-	-23.618338	-46.635497	-	Passive	PUF	-	3 months	3 months	2018
GAPS	Chile	Concepción	GR28	-	-36.475200	-73.031900	30	Passive	PUF	-	3 months	3 months	2015
GAPS	Chile	Santiago	-	-	-33.468782	-70.596188	-	Passive	PUF	-	3 months	3 months	2018
GAPS	Colombia	Arauca	GR04	Rural	7.045770	-70.444059	2	Passive	PUF	-	3 months	3 months	2004
GAPS	Colombia	Bogota	-	-	4.636833	-75.083444	-	Passive	PUF	-	3 months	3 months	2018
GAPS	Colombia	Manizales	GR22	Remote	5.075833	-75.436669	2670	Passive	PUF	-	3 months	3 months	2011
GAPS	Costa Rica	Tapanti National Park	GR03	-	9.695733	-83.865354	2830	Passive	PUF	-	3 months	3 months	2004
GAPS	Ecuador	Quito	GR19	Urban	-0.250000	-78.583334	1658	Passive	PUF	-	3 months	3 months	2011
GAPS	Ecuador	Santa Cruz Island	GR13	-	-0.978458	-89.359129	168	Passive	PUF	-	3 months	3 months	2008
GAPS	Mexico	Celestún / Yucatan	GR17	-	20.859201	-90.392400	52	Passive	PUF	-	3 months	3 months	2010
GAPS	Mexico	Mexico City	-	-	19.246470	-99.101350	-	Passive	PUF	-	3 months	3 months	2018
GAPS	Mexico	Valley of the Yaqui / Sonora	GR16	Agricultural	27.127308	-109.840471	140	Passive	PUF	-	3 months	3 months	2010
LAPAN	Antigua & Barbuda	Antigua & Barbuda	71	Suburban	-17.100000	-61.838889	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Argentina	Bahia Blanca 1	22	Suburban	-38.775889	-62.005278	-	Passive	XAD	-	1 year	1 year	2010
LAPAN	Argentina	Bahia Blanca 2	23	Suburban	-38.699528	-62.444722	-	Passive	XAD	-	1 year	1 year	2010
LAPAN	Argentina	Puerto Madryn	52	Urban	-42.808083	-65.043889	-	Passive	XAD	-	1 year	1 year	2010

Site details								Sampling details					
Network	**Country**	**Name**	**Network ID**	**Background Type**	**Latitude**	**Longitude**	**Elevation**	**Sampler**	**Type**	**Volume**	**Duration**	**Frequency**	**Since**
LAPAN	Argentina	Rio Gallegos	30	Urban	-51.647306	-69.207222	-	Passive	XAD	-	1 year	1 year	2010
LAPAN	Argentina	Salta	76	Suburban	-24.633544	-65.166944	-	Passive	XAD	-	1 year	1 year	2017
LAPAN	Argentina	Viedma	25	Agricultural / Suburban	-40.898750	-62.881389	-	Passive	XAD	-	1 year	1 year	2010
LAPAN	Argentina	Villa Regina	26	Agricultural / Suburban	-39.102333	-67.108333	-	Passive	XAD	-	1 year	1 year	2010
LAPAN	Brazil	Abrolhos Island	1	-	-17.968317	-38.684444	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Brazil	Araraquara, SP	31	Urban / Agricultural	-21.791944	-48.181111	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Brazil	Barretos, SP	65	Urban	-20.572461	-48.574167	-	Passive	XAD	-	1 year	1 year	2015
LAPAN	Brazil	Belém, PA	18	Urban	-1.474158	-48.458333	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Brazil	Botanical Garden, POA, RS	72	Urban	-30.053686	-51.174722	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Brazil	CETESB, SP	2	Urban	-23.561097	-46.701389	-	Passive	XAD	-	1 year	1 year	2010
LAPAN	Brazil	Chapada dos Veadeiros, GO	3	-	-14.066708	-47.461389	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Brazil	Cristalino State Park, MT	14	-	-9.597813	-55.932222	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Brazil	Curitiba, PR	4	Urban	-25.449750	-49.234167	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Brazil	Diamantino, GO	5	Agricultural	-14.129678	-57.656111	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Brazil	Fortaleza, CE	8	Urban	-3.744817	-38.573889	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Brazil	Iguaçu National Park, PR	41	-	-25.626736	-54.478611	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Brazil	Itatiaia National Park, RJ	43	-	-22.385833	-44.678889	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Brazil	Limeira, SP	44	Urban	-22.562233	-47.422222	-	Passive	XAD	-	1 year	1 year	2015
LAPAN	Brazil	Manaus, AM	10	-	-2.594611	-60.209220	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Brazil	Moeda, MG	68	-	-20.352322	-43.952500	-	Passive	XAD	-	1 year	1 year	2017
LAPAN	Brazil	Nova Nazaré. MT	-	Rural	-13.958611	-51.776944	-	Passive	XAD	-	1 year	1 year	2017
LAPAN	Brazil	Pico do Jaraguá, SP	49	Suburban / Remote	-23.456314	-46.766111	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Brazil	Porto Alegre, RS	11	Urban	-30.034553	-51.233333	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Brazil	Porto Velho, RO	20	Urban	-8.836186	-63.938889	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Brazil	Puruzinho, AM / Puruzinho Lake	12	-	-7.370556	-63.059440	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Brazil	Recife, PE	13	Urban	-8.052883	-34.950000	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Brazil	Rio de Janeiro, RJ	7	Urban	-22.878533	-43.246111	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Brazil	Rio Grande, RS	9	Suburban	-32.068906	-52.161389	-	Passive	XAD	-	1 year	1 year	2010
LAPAN	Brazil	Rocas Atoll / Atol das Rocas	32	-	-3.856417	-33.817420	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Brazil	São José dos Ausentes, RS	16	Remote	-28.594170	-49.818590	-	Passive	XAD	-	1 year	1 year	2010
LAPAN	Brazil	São Luis do Maranhão, MA	17	Suburban	-2.593833	-44.211111	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Brazil	São Pedro & São Paulo Archipelago	-	-	0.959203	-29.352500	-	Passive	XAD	-	1 year	1 year	-

Site details								Sampling details					
Network	**Country**	**Name**	**Network ID**	**Background Type**	**Latitude**	**Longitude**	**Elevation**	**Sampler**	**Type**	**Volume**	**Duration**	**Frequency**	**Since**
LAPAN	Brazil	Souré, PA	-	Rural	-0.695086	-48.496389	-	Passive	XAD	-	1 year	1 year	2017
LAPAN	Brazil	Trindade Island	59	-	-20.508140	-29.312140	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Brazil	Vitória, ES	21	Urban	-20.292603	-40.296111	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Bolivia	Chacaltaya	27	-	-16.350356	-68.131667	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Chile	Concepcion	36	Urban	-36.857950	-72.948333	-	Passive	XAD	-	1 year	1 year	2014
LAPAN	Chile	Cordilheira Darwin	-	-	-54.414400	-70.915556	-	Passive	XAD	-	1 year	1 year	2016
LAPAN	Chile	Torres del Paine	66	-	-50.980633	-73.189167	-	Passive	XAD	-	1 year	1 year	2016
LAPAN	Chile	Antarctica	-	-	TBD	TBD	TBD	Passive	XAD	-	1 year	1 year	2018
LAPAN	Chile	Antofagasta	-	Urban	-23.613611	-70.383889	-	Passive	XAD	-	1 year	1 year	2018
LAPAN	Chile	Coyaique	-	-	-45.578750	-71.436389	-	Passive	XAD	-	1 year	1 year	2018
LAPAN	Chile	Juan Fernandez Island	-	-	-33.632222	-78.860556	-	Passive	XAD	-	1 year	1 year	2018
LAPAN	Chile	Valle Alegre	-	Rural	-32.807778	-71.436944	-	Passive	XAD	-	1 year	1 year	2018
LAPAN	Colombia	Arauca	-	Agricultural	7.012714	-70.744722	-	Passive	XAD	-	1 year	1 year	2017
LAPAN	Colombia	Leticia	63	-	-4.191528	-69.939444	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Colombia	Reserva Natural Rio Blanco / Manizales	64	-	5.000000	-75.736111	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Colombia	Universidad de Cartagena	55	Urban	10.402806	-75.505833	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Costa Rica	Biolley de Buenos Aires / Puntarenas	70	-	9.044722	-83.029722	-	Passive	XAD	-	1 year	1 year	2016
LAPAN	Ecuador	Machadilha National Park	-	-	-1.538356	-80.676111	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Ecuador	Manglares Ecological Reserve	-	-	1.374397	-78.949167	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Honduras	Tegucigalpa	28	Urban	14.097500	-87.202778	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Panama	Santiago	67	Suburban	8.127972	-80.989444	-	Passive	XAD	-	1 year	1 year	2016
LAPAN	Peru	Chaclacayo, Lima	-	Suburban	-11.972500	-76.754444	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Peru	PUCP, Lima	73	Urban	-12.073331	-77.079722	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Peru	Tambopata Research Centre / Puerto Maldonado	74	Rural	-12.833470	-69.292250	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Uruguay	Montevido	46	Urban	-34.882942	-56.164167	-	Passive	XAD	-	1 year	1 year	2010
LAPAN	Uruguay	Salto	54	Rural / Agricultural	-31.474450	-57.099410	-	Passive	XAD	-	1 year	1 year	2010
LAPAN	Venezuela	IVIC Caracas	29	Suburban	10.395970	-66.985390	-	Passive	XAD	-	1 year	1 year	-
LAPAN	Venezuela	UCV Caracas	75	Urban	10.485975	-66.893889	-	Passive	XAD	-	1 year	1 year	-

Note: Many of the sites listed in the China and East Asian POPs networks are inactive but will be re-deployed for the next GMP data collection.

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

Training videos:

Mounting and deployment of PUF disk samplers, by AMETEC-UNU:
https://www.youtube.com/watch?v=pkz48SyIzXw
Instructions on PUF disk sample changes for Arctic passive network:
https://www.youtube.com/watch?v=8A22nvu7kbQ
XAD tube sampler setup: https://www.youtube.com/watch?v=9vvrvpRD96k&feature=youtu.be
Temperature logger installation: https://www.youtube.com/watch?v=nkzbCzRPMyc&feature=youtu.be
PUF passive sampling video (in Arabic): https://www.youtube.com/watch?v=NznXwa-xk-0

List of Protocols available from the GAPS Network:

Protocols for PUF disk sampler:

Cleaning PUF disk sampler housing
Preparing PUF disks for passive air sampling
PUF & SIP disk sampler installation and deployment for GAPS
SIP disks – Protocol fro preparing sorbent impregnated PUF (SIP) disks for passive air sampling (GAPS network) using ASE

Protocols for XAD sampler:

GAPS Insrtructions for XAD sampler

Part III Additional Considerations for Air Sampling

Toxicity of Chemical Mixtures in Air: Cumulative Effects: A recommendation from the second GMP report was that more attention should be given to cumulative effects and the toxicity of the mixture of chemicals in air. This is to acknowledge that humans and ecosystems are exposed to an increasing number of chemicals and that only a small fraction of these are capable of being measured in air and tracked under the GMP. Therefore, in order to address the core mandate of the Stockholm Convention for protecting human health and the environmental from the harmful effects of POPs it is important to explore and better understand the combined effects of chemicals in air while continuing to monitor the chemicals that until now have been identified as POPs. Considerable advances have been made in recent years to link air monitoring and toxicological assessment for chemicals mixture in air (e.g. Cupr et al., 2006, 2013; Novak et al., 2013, 2014; Ersekova et al., 2015; Jariyasopit et al., 2016).

Use of tree rings and other natural archives for deriving historic trends of POPs: Over the past several years, researchers have shown that tree wood can acts as a passive sampler for air and that cores can be sampled from trees (without harming the tree) to investigate historical trends of POPs in the tree rings (e.g. Kuang et al., 2011; Odabasi et al., 2015; Rauert et al., 2016). Rauert et al.(2018) have characterized the uptake potential of POPs by tree wood in an effort to use tree rings data to semi-quantitatively reconstruct historic chemical profiles and patterns in air. This approach shows promise for assessing temporal trends of POPs in locations where no air sampling has occurred in the past (i.e. no sample archives). However, more work is needed to better characterize the parameters that impact uptake and how uptake may vary with meteorology, tree species and other relevant factors.

Other indirect methods for reconstructing long term historic trends of POPs in air include natural archives such as sediment cores, peat cores, and even ice cores (e.g. Muir et al., 2013). Although these techniques should not be considered as a replacement for air monitoring, they can contribute useful information and provide insight to POPs levels in regions where no data exist or prior to the onset of an air sampling network.

Indoor sampling: Although indoor sampling is not a requirement of the GMP, a comparison of indoor vs outdoor levels of POPs can be useful for understanding sources to ambient air and for identifying potential contamination to nearby outdoor sampling sites. (e.g. Melymuk et al., 2016). This is especially relevant for many of the new POPs that are used in commercial products that occur indoors and which may exhibit orders of magnitude higher concentrations in indoor air compared to ambient air. Assessment of indoor air as a route of human exposure is also relevant to the interpretation of human tissue data on POPs and related temporal trends (Section 4.2). Herkert et al. (2018), Bohlin et al. (2014b) and others have critically evaluated the application of the PUF disk sampler in the indoor environment and provide guidance for future work.

ANNEX 3 TO THE GUIDANCE

Summary information on the UNEP/WHO Survey on Human Milk under the Global Monitoring Plan for POPs

The UNEP/WHO human milk survey aims at measuring persistent organic pollutants (POPs) in human milk according to the requirements of Article 16 of the Stockholm Convention on POPs, for generating comparable monitoring data over time in support of the effectiveness evaluation of the Convention. The survey is jointly implemented by the Secretariat of the Stockholm Convention, the World Health Organization (WHO) and UNEP's Division of Technology, Industry and Economics (DTIE), Chemicals Branch.

A harmonized comprehensive protocol and guidelines have been developed by WHO (WHO, 2007) and amended by UNEP (last amendment: see UNEP, 2017a), providing methodological guidance to countries in implementing the survey, including preparation of the national protocol according to needs at national level. Participating countries are encouraged to adhere as closely as possible to the protocol, which provides guidance on the number and type of samples, selection of donors, collection, storage and pooling of samples, and shipping of samples to the reference laboratory. All samples are analysed in the WHO/UNEP reference laboratory, the State Institute for Chemical and Veterinary Analysis of Food (CVUA) in Freiburg, Germany. Proteinophilic POPs (e.g. PFOS) are analyzed at MTM Orebro in Sweden.

In the implementation of the survey, the following principles should be followed:

- Breastfeeding should be protected, promoted and supported;
- The health benefits of breastfeeding to both mother and baby should be clearly and consistently communicated;
- Sampling of milk should not be an undue burden on the mother nor should it compromise the nutritional status of the infant.

A summary of the guidelines is provided below.

A national coordinator should be selected and be responsible for the overall planning and implementation of the survey in the country, assisted by health, laboratory and administrative staff.

Selection criteria for donating mothers: first child mother, 3-4 weeks after the birth, breastfeeding one child only. The most important criterion to be met is for donors to be first time mothers.

Number of donors: In order to get statistically reliable data, an appropriate number of individual donors must be recruited to provide samples for the survey. As a first approximation, a minimum of 50 individual samples is recommended for each country. Equal aliquots of these individual samples are mixed to form a representative composite sample ("pooled sample"). The power of the survey can be increased by the inclusion of more than 50 individual samples and is encouraged. It is recommended to collect one representative individual sample per one million citizens. In particular, countries with populations greater than 50 million should include at least one additional participant per one million population over 50 million. Countries with populations well over 50 million (or with sufficient resources) are encouraged to prepare a second pooled sample (or more) if feasible.

Strategies for selecting donors: Given the time constraints for sample collection, interviewing of potential donors should take place at post-natal or well-baby clinics. The stratification of participants should follow the same principles as in the previous survey.

Glassware for collection of samples:
Sterilized glassware will be provided to participating countries for the collection of the individual samples and the preparation of the pooled sample by the WHO/UNEP reference laboratory, CVUA Freiburg.

Collection of samples: It is recommended that sampling being carried out between three to eight weeks (21 days to two months) after delivery. At the time of sample collection, individual interviews should be used to

complete the information in the participant questionnaire. At least 50 ml of milk in total should be collected. The sample should be collected directly to the collecting jar and stored in the freezer until it can be shipped.

Preservation of collected samples: The samples shall be preserved via freezing (storage in the refrigerator at about 4 °C for a maximum of 72 hours, or for a longer time period in the freezer at -20 °C) or by addition of potassium dichromate.

Sample analysis: After the collection of 50 individual samples (50 ml each), the following procedures are applied:

- **Preparation of the pooled sample:** To prepare the pooled sample, each individual milk sample shall be homogenized by shaking for 5 minutes: The 50 ml sample will be split into two portions of 25 ml each: One bottle of 25 ml will constitute the national individual sample and remain in the country (see point 2 below); the second 25 ml are put into a 2000 ml glass bottle to prepare the pooled sample (50 x 25 ml = 1250 ml pooled sample);

- **Individual samples**: Individual 25 ml of human milk can be stored by the country (see above) for the analysis of selected POPs according to national capability. It is recommended that POPs laboratories wishing to analyse national human milk samples to strengthen their analytical capacity have participated/are participating at interlaboratory studies such as the "Biennial Global Interlaboratory Assessment on Persistent Organic Pollutants" organized by UNEP where also reference samples can be obtained.

Any remaining milk from individual samples should be pooled and sent to the WHO Global Human Milk Bank through the WHO reference laboratory.

Each individual and pooled sample should be labelled with a unique identification code. The storage and shipment of all samples should be deep-frozen.

The pooled milk sample shall be sent to the WHO/UNEP reference laboratory for analysis of all POPs listed in the Stockholm Convention. The pooled samples shall be accompanied by the completed summary of information.

ANNEX 4 TO THE GUIDANCE

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

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

Material

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

Sampling

The sampling protocol includes the following:

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

Storage

If samples are sent to the laboratory within 5 days :

Keep at 4 °C until shipped.

If samples are kept for more than 5 days :

Keep at – 20 °C until shipped.

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

Shipping

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

Send samples early in the week to the following address:

Laboratoire de la toxicologie
Centre de toxicologie / INSPQ
945 avenue Wolfe
4ème étage
Québec, QC
G1V 5B3
Phone : (418) 650-5115 ext 5100

ANNEX 5 TO THE GUIDANCE

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

Listed Chemical	Representative Analyte in water	Water solubility[1] (mg/L) at 25ºC	Log Kow	Log Koc[2]	Ref[3]
Aldrin	Aldrin	0.02	3.0	2.6	1
Chlordane	*cis*-chlordane	0.056	6.0	5.5	1
Chlordecone	Chlordecone	2.7	4.5	3.4	2
DDT	4,4'-DDT	0.0055	6.2	5.4	1
	4,4'-DDE	0.04	5.7	5.0	1
Dieldrin	Dieldrin	0.17	5.2	4.1	1
Endrin	Endrin	0.23	5.2	4.0	1
Endosulfan	a-Endosulfan	0.5	4.9	3.6	2,3
	Endosulfan sulfate	0.22	3.6	3.2	2,3
HCB	HCB	0.005	5.5	5.0	1
Pentachlorobenzene	PeCBz	0.65	5.0	4.5	1
Heptachlor	Heptachlor epoxide	0.35	5.0	4.0	1
Hexabromobiphenyl	HBB	0.011	6.4	5.9	4
Hexachlorocyclohexanes	α-HCH	1.0	3.8	3.8	1
	β-HCH	7.3	3.7	3.0	1
Mirex	Mirex	$6.5x10^{-5}$	6.9	6.0	1
Perfluorooctane sulfonate (PFOS)	PFOS	680	-	2.6	5,6
Polychlorinated biphenyls (PCB)	PCB 28	0.16	5.8	5.3	1
	PCB 52	0.03	6.1	5.6	1
	PCB 101	0.01	6.4	5.9	1
	PCB 153	0.001	6.9	6.4	1
Polychlorinated dibenzo-*p*-dioxins (PCDD)	TCDD	$1.93x10^{-5}$	6.8	6.3	1
Polychlorinated dibenzofurans (PCDF)	TCDF	$4.19x10^{-4}$	6.5	6.0	1
Toxaphene	P26	-	5.5	5.0	7
	P50	-	5.8	5.3	7
Pentabromo diphenyl ethers	BDE 47	0.011	6.8	6.3	8,9
	BDE 99	0.0024	7.3	6.8	8,9
Octabromo diphenyl ethers	BDE 183	-	8.3	7.8	9

[1]Water solubility of the solid and reported in mg/L
[2]Koc estimated from Seth et al (1999)
[3] References cited in Section 4.2.1.: 1. Mackay et al (2006); 2 ATSDR (2000); 3.Weber et al. (1997);4 USEPA (2008); 5 UNEP (2006); 6 Higgins and Luthy (2006); 7 Muir et al (2006); 8 European Commission (2001); 9 Braekevelt et al. (2003). Full references cited in Section 4.2.1.

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IADN https://www.epa.gov/great-lakes-monitoring/great-lakes-integrated-atmospheric-deposition-network

Lancaster Environment Centre http://www.lec.lancs.ac.uk/

MONET / RECETOX / GENASIS database http://www.recetox.muni.cz/index-en.php; http://www.genasis.cz/index-en.php

University of Toronto (Wania Group) http://www.utsc.utoronto.ca/~wania/main.html

Global Atmsopheric Watch (WMO/GAW)http://www.wmo.int/pages/prog/arep/gaw/gaw_home_en.html

Training videos

Mounting and deployment of PUF disk samplers, by AMETEC-UNU: https://www.youtube.com/watch?v=pkz48SyIzXw

Instructions on PUF disk sample changes for Arctic passive network: https://www.youtube.com/watch?v=8A22nvu7kbQ

XAD tube sampler setup: https://www.youtube.com/watch?v=9vvrvpRD96k&feature=youtu.be

Temperature logger installation: https://www.youtube.com/watch?v=nkzbCzRPMyc&feature=youtu.be

PUF passive sampling video (in Arabic) https://www.youtube.com/watch?v=NznXwa-xk-0

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Published by the Secretariat of the Stockholm Convention on Persistent Organic Pollutants in January 2021. For more information please contact:

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