Appendix 2:

POPs monitoring in developing countries, optimization, intercalibration and accreditation for delivering high quality data

Acknowledgement

This report was coordinated by the Chemicals and Health Branch of the United Nations Environment Programme (UNEP) in the framework of the Global Environment Facility-funded POPs Global Monitoring Plan projects in the Africa, Asia, Pacific and Latin America and the Caribbean regions (Project GEF ID 4881, 4886, 4894, 6978).

This document has been prepared by:

Jacob de Boer

Internal review at UNEP was conducted by Victor Hugo Estellano, Haosong Jiao, Tapiwa Nxele The report has been produced with the financial assistance of the Global Environment Facility.

Table of Contents

Арре	endix 2:		1
A	cknowle	dgement	2
Si	ummary		4
Part	1: Intero	alibration, accreditation and certification of POPs analysis for delivering high quality data	5
1.	. Intro	duction	5
2.	. Inter	laboratory studies and CRMs	7
	2.1.	Certified Reference Materials (CRMs)	8
3.	. Accr	editation	9
	3.1.	Accreditation bodies	9
4.	. Inter	views	. 10
	4.1.	IAEA Marine Laboratory	. 10
	4.2.	QUASIMEME	. 11
	4.3.	Stakeholders	. 11
5.	. Disc	ussion	. 12
6.	. Cond	clusions and recommendations	. 14
7.	. Refe	rence	. 15
Part the S	2: Towa Stockhol	rds optimizedPOPs monitoring in developing countries to support the effectiveness evaluation o m Convention	f 17
1.	. Intro	duction	. 17
2.	. Com	parison with other monitoring programmes and the needs of developing countries	. 17
	2.1.	Other monitoring programmes on POPs	. 17
	2.2.	The role and needs of developing countries	. 20
3.	. Key	actors for optimal POPs monitoring in developing countries	. 21
	3.1.	Responsibilities and commitment of authorities	. 21
	3.2.	Equipment	. 21
	3.3.	Costs	. 22
4.	. Build	ling a new monitoring programme	. 23
	4.1.	The interlaboratory studies	. 24
	4.2.	Matrices	. 24
	4.3.	Target compounds	. 27
	4.4.	Locations	. 29
	4.5.	Modelling options	. 30
5.	. Reco	mmendations	. 31
6.	. Liter	ature	. 31

Summary

The objective of the Stockholm Convention on Persistent Organic Pollutants (POPs) is to protect human health and the environment from POPs. The global monitoring plan (GMP) under the SC was designed to assess the effectiveness of the SC in globally reducing POPs.

Part 1 of this report formulate answers on questions about quality assurance/quality control of the analysis of persistent organic pollutants (POPs), such as about accreditation and interlaboratory studies, with the aim to assist POPs laboratories in developing countries in their analytical work and enhance the quality of their POPs data. An overview of accreditation bodies and interlaboratory study organizers for POPs analysis is given. Several recommendations could be formulated. Stakeholders emphasize the need for a continuation of the POPs interlaboratory studies as organized by UNEP. Some stakeholders ask for even an expansion of the number of matrices. On the other hand, substantial costs savings can be realized in trimming these exercises back in number of POPs, matrices, and participants. Accreditation bodies do not organize interlaboratory studies. They can accredit a laboratory, once that laboratory is able to demonstrate that its analytical results always meet predefined criteria. The most essential tool to demonstrate this are interlaboratory studies in which the laboratory participates and demonstrate good results. Such interlaboratory are normally organized by proficiency testing scheme providers. Training of laboratories needs to be organized by offering longer training periods for laboratory staff members. Preferably, that model should first be tried with one or two laboratories per continent, that could later possibly act as regional expert laboratory. POPs laboratories could possibly learn from food laboratories and the activities in this field by FAO. Due to legislation and customs requirements, food laboratories seem to be better organized than environmental laboratories.

Part 2 of this report learn lessons from the recent UNEP/GEF GMP projects on POPs monitoring to see where improvements in terms of quality and cost-effectiveness can be installed prior to a new round of monitoring. OtherPOPs monitoring programmes such as the Arctic Monitoring and Assessment Programme (AMAP), the Global Atmospheric Passive Sampling Network (GAPS), and the Monitoring Network (MONET) make a very useful contribution to the GMP data warehouse, however several data gaps on geographical and temporal coverage, mostly in developing countries still exist. There is currently no role for developing countries other than in sampling. As in the successful POPs in human milk monitoring programme, GAPS and MONET deliver data that are all analysed in centralized laboratories. To improve that situation in developing countries, it is recommended to install a capacity building programme. This, however, can only be successful if the following two conditions can be met, i) a full commitment of the authorities responsible for the participating laboratories, and ii) ensuring capacity of well-functioning mass spectrometers in the participating laboratories. A meeting to achieve the latter condition with donors, mass spectrometry companies, scientists and UNEP representatives is highly recommended. It is also recommended to continue with the global interlaboratory studies with a frequency of once per two years, but in a much-reduced scheme only focusing on air and human milk. Options for a focused monitoring programmne, such as reduction of the number of locations, lowering the sampling frequency and reduction of the number of POPs to be analysed, and improvement of the air sampling quality are given to make the next monitoring programme more cost-effective, while the quality of the data will be improved. Finally, a study on modelling to predict environmental concentrations of POPs starting from production volume data, taking polychlorinated biphenyls (PCBs) as an example, is recommended.

Part 1: Intercalibration, accreditation and certification of POPs analysis for delivering high quality data

1. Introduction

The Stockholm Convention needs background data on persistent organic pollutants (POPs) in the environment to follow the trends of these contaminants and to evaluate the effectiveness of measures and actions undertaken by the Parties to the Convention.POPs concentrations are therefore monitored on a regular basis, by various networks, and laboratories at national regional and global scales. ThePOPs concentrations, used by the effectiveness evaluation, are measured within the framework of a global monitoring plan (GMP), in core matrices being air, human milk or human blood, and water (only for PFAS). Analysis of POPs is never simple. It requires a high sensitivity and selectivity and, therefore, sophisticated, and rather expensive instrumentation, and several relatively complicated steps, such as extraction, cleanup, and instrumental analysis, that all contribute to the overall uncertainty of the final result. This uncertainty should, however, not be too high, as trends inPOPs concentrations need to be determined within a maximum uncertainty of ca. 50%, but preferably lower. Because various laboratories provide data for the Convention, an additional uncertainty is added to the data, because differences in performance of laboratories always exist. Those differences should of course be as small as possible. Consequently, the challenge is to ensure high quality accuratePOPs concentrations per laboratory, and to minimize the variation in data among the laboratories that provide data to the Convention.

Laboratories have several tools to their disposition to ensure the quality of their data. These tools are summarized under the concept Quality Assurance/Quality Control (QA/QC). QA stands for 'All actions carried out to plan the proper performance of the analytical task'; QC for 'All operational techniques and activities that are used to fulfil requirements for quality'. Two of the most important concepts within QA/QC are Precision and Trueness.

- Precision can be checked in the laboratory by e.g., analyzing a specific sample (a so-called laboratory reference material or LRM) a certain number of times and determining the variation in the results. An LRM is a large batch of homogeneous material, e.g., fish or sediment or milk, of which a sub-sample is also analysed, once the method has been set-up, in each series of samples to check if the analytical results are stable. Such a material is essential for eachPOPs laboratory. The results of the LRM analyses are plotted in a so-called quality control (QC) chart.
- Trueness can only be determined by external comparisons. This can be done by using a certified reference material (CRM) or by participating in interlaboratory studies.

A CRM is a reference material that is certified by a group of expert laboratories for certain contaminant concentrations with a given uncertainty. Although this a valuable tool, a drawback is that CRMs come with a certificate, from which the certified values can be read before the analysis is carried out. That might bias the analyst towards the right answer. Therefore, interlaboratory studies are the only real blind tests in which the participating laboratories must analyse one or more unknown samples in which the concentrations of the target analytes are unknown. If successful, the laboratory can use the interlaboratory test results data as a proof of the quality of their analysis to solicitate an accreditation body to give a certificate of accreditation. However, not only the interlaboratory test result will convince the accreditation body. To obtain good results in an interlaboratory study and in their daily analyses, the laboratory must build an entire quality system (Figure 1).

Some examples of what needs to be included in a file to ask for an accreditation from and accreditation body are: a detailed description of the instruments, e.g., gas chromatograph (GC), mass spectrometer (MS), etc., but also smaller instruments, detailed analytical method descriptions, description of the management of the laboratory, description of the data flow, validation of excel sheets, registration file of temperatures of refrigerators and freezers, registration of balance calibrations, etc. The entire file must be offered to the accreditation body,



Quality System of Laboratory

Figure 1. Overview of a quality system of a proper functioning laboratory, as required for accreditation.

which will scrutinize it to check if the accreditation can be given. The amount of work to obtain an accreditation is truly substantial and is most likely underestimated by manyPOPs laboratories in developing countries. Laboratories in developed countries normally need 1-2 years before they can offer a complete file to the accreditation body. Once the accreditation has been assigned, each year the assessment will be repeated to check if the laboratory maintains the same level of quality. Accreditation bodies will always ask if the laboratory has participated in national or international interlaboratory studies. If such studies are available for the target analyte, participation is mandatory to maintain the accreditation.

Until now, several experienced laboratories have contributed POPs data to the GMP. However, one of the aims of the Stockholm Convention is to broaden the responsibility for generating POPs monitoring data to a larger group of laboratories, including laboratories in developing countries. Accreditation is a great help in assuring comparable data. However, until now very fewPOPs laboratories have obtained an accreditation. Even some of the larger contributors of data to the GMP may not be accredited. University laboratories are for example often not accredited because their work does not have a routine character. Nevertheless, if laboratories have done a proper validation and determined the precision and trueness of their method, data can still be comparable and may be used for the GMP or other purposes. It is, therefore, essential to organize interlaboratory studies for POPs analyses. Only then it can be seen which laboratories are good enough and produce reliable data that can be used for establishing temporal and spatial trends within the GMP.

During the first UNEP/GEF GMP projects rounds, four international interlaboratory studies were organized (Fiedler et al., 2022). In addition, circa 50 laboratories received UNEP-sponsored training by experts inPOPs analyses. Standard operating protocols have been prepared for all laboratories, and guidelines with technical advice were provided to all participants of the interlaboratory studies. In this way a so-called learning exercise was offered to all participants, during which the laboratories could learn from the guidelines and from their results, to improve their methods in the next round. Unfortunately, the results of these four interlaboratory studies showed a different outcome. Although at the level of individual laboratories some progress was made, most laboratories failed in improving their results. As a group of laboratories, improvement was absent, with an exception for dioxin laboratories, PBDE and air results. Dioxin laboratories are, however, mainly situated in the western world. The main reasons for this undesired result was: i) there were many new laboratories in most of the rounds, which blurred a possible improvement made by other laboratories (inexperienced laboratories do generally not perform very well), ii) the training was not as successful as was hoped, iii) a large number of laboratories were only or mainly active during the interlaboratory studies; a regular flow of samples through those laboratories does not exist, and iv) authorities did not invest in training, consumables and equipment.

The four interlaboratory studies organized along the UNEP/GEF GMP projects work were all large in terms of number of target compounds, number of matrices and number of participants (Fiedler et al., 2022). There have probably not been larger interlaboratory studies on POPs in the world than these four exercises. That has resulted in a very large and valuable dataset. However, costs associated with these exercises were very high, around 1 million US dollar for the four rounds together for the organization alone, apart from funding for the participation of a large number of laboratories. The need for offering laboratories, and especially those in developing countries, a possibility to check theirPOPs data in regular blind test is beyond doubt. However, there are questions regarding the costs associated with the organization, the size and frequency of the exercises, about the umbrella under which these studies should be carried out and questions regarding accreditation. The objective of this report is to give answers on these questions with the aim to assistPOPs laboratories in developing countries in their analytical work and enhance the quality of theirPOPs data and assist UNEP in building a dataset with reliable data only.

2. Interlaboratory studies and CRMs

The European Proficiency Testing Information System (EPTIS) database (EPTIS, 2023) contains all interlaboratory studies known in many different fields, from cosmetics to pulp and paper and petroleum products. To reduce the large amount of information, we will only focus on interlaboratory studies for POPs in environmental matrices. Even then, many studies can be found. Those studies vary in size, objective, and frequency. There are one-off studies which can be organized for a specific, often scientific reason (e.g., Krätschmer and Schächtele, 2019), learning exercises as outlined above to bring laboratories at a certain level of performance, and proficiency testing (PT) schemes that organize interlaboratory studies on a regular basis and are useful for laboratories with an accreditation. Learning exercises are organized by QUASIMEME (Quality Assurance for Marine Environmental Matrices in Europe) when a new contaminant group is added to for the first time. The results are often discussed in a workshop with all participants. The UNEP/GEF interlaboratory studies, such as the last four that were organized between 2010 and 2022, are also examples of learning exercises. A number of laboratories was trained, expert advice was given on how to treat the samples of the study and the results were discussed in a workshop with all participants.

Food laboratories are generally well-organized. Food and environmental laboratories normally have fish in common. Most interlaboratory studies on POPs in food include fish, fish oil or shellfish. There are several interlaboratory studies on organic contaminants in food and feed, organized on a regular

basis. The National Reference Laboratories (NRLs) for halogenated POPs in feed and food from EU member states are requested to participate as part of their work programme. NRLs are also invited to encourage the participation of Official Laboratories from their member states (EU, 2017). The evaluation of results is performed according to ISO 13528:2022 and the International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories (This is a cooperation of international standardizing organizations—AOAC International, ISO, and IUPAC). At the end of the PT, a certificate is issued to each participant. ThesePOPs interlaboratory studies in feed and food are organized by the European reference laboratory in Freiburg, Germany (EURL, 2023). Other interlaboratory studies on POPs in food are for example organized by the Norwegian Institute of Public Health (Bruun Bremnes et al., 2021) and FAPAS (UK) (FAPAS, 2023).

The International Atomic Energy Agency (IAEA), Vienna, Austria, through their Marine Laboratory in Monaco, organizes relatively large interlaboratory studies on marine contaminants, trace elements, radionuclides and organic contaminants in seawater, fish, and sediment (IAEA, 2022). The frequency is about once per 3-5 years for POPs, while studies on trace metals and radionuclides have been organized more frequently. The last study on POPs had 50 participating laboratories from 28 countries, but no countries from east and southeast Asia and the Pacific and only one from South America (IAEA, 2022). Only one fish sample was sent to the laboratories. The results of the IAEA studies are often used for certifying the used test material. This is helpful for the member countries of IAEA, although the uncertainties are normally larger than those in certified reference materials (CRMs) produced by professional CRM producers like the National Institute for Standards (NIST), USA, and the European Joint Research Centre (JRC) in Geel, Belgium.

QUASIMEME is another PT provider that focuses on the marine environment. It provides PTs for a large group of contaminants such as POPs, trace elements, nutrients, marine toxins, and others in a variety of matrices such as fish, shellfish, seawater, and sediment. The frequency of most studies is twice per year. All results are kept in a database and from time-to-time information on long-term variation in laboratories comes available. Workshops on new contaminants and specific analytical topics are regularly organized. Related to QUASIMEME is WEPAL, also based in Wageningen, The Netherlands. They organize PTs for trace elements and POPs in soil with a frequency of four times per year. The number of participants in the QUASIMEME and WEPAL exercises varies between ca. 10 and 100 per exercise. Participation is not limited to Europe.

The QUASIMEME and WEPAL studies and the ones organized by NIPH (Norway) and FAPAS (UK) are commercial exercise. That means that there is a fee for the participation. The fees vary between ca. 300-500 Euro per year (two exercises per contaminant/matrix combination) in QUASIMEME and FAPAS to 1500 Euro for four food items in the NIPH study. QUASIMEME and WEPAL might consider reduced fees for developing countries. There are many morePOPs interlaboratory studies. Many are one-off studies, or studies on only a national scale or even within projects such as European research projects. Many others are PT schemes, organized on a commercial basis, i.e., a fee must be paid for participation. Information can be found in the EPTIS database (EPTIS, 2023).

2.1. Certified Reference Materials (CRMs)

CRMs are the golden standard for chemical analyses. They can be compared to the platinum meter in Paris for length. Only highly specialized organizations produce CRMs, also for POPs analyses. The most known ones are the National Institute for Standards and Technology (NIST), USA, The European Joint Research Centre (JRC), Geel, Belgium, the National Research Centre (NRC), Ottawa, Canada, and the Bundesanstalt für Materialforschung und -prüfung (BAM), Germany. To produce a CRM, expert laboratories in the field are invited to carry out a series of replicate analyses of a sample from a large batch of homogeneous and stable material. Based on the results and after a deep technical

evaluation certified values and their uncertainties are being assessed and included in a certificate. Other laboratories can order these materials to check the trueness of their methods. CRMs are very important and should be used on a regular basis by all POPs laboratories as an essential QC tool *in addition* to their participation in interlaboratory studies.

3. Accreditation

Accreditation is defined as 'the independent evaluation of conformity assessment bodies against recognised standards to carry out specific activities to ensure their impartiality and competence'. Accreditation of a laboratory means that a laboratory guarantees that the data produced have an uncertainty within a pre-defined range and the determination of the analyte was carried out according to a validated method, laid down in a fixed protocol. With validation, we mean that the method was tested for its repeatability (e.g., six or eight analyses of one sample (this can be the LRM) carried out on one day, by one analyst), reproducibility (six or eight analyses of the LRM on different days, if possible by different analysts and, if available, on different instruments), and robustness (sensitivity of method for minor changes in protocol, e.g., change of ambient temperature in the laboratory, influence of light on samples, storage time of extracts, etc.). Accreditations can be given per analyte/matrix combination, or for analytes in a range of matrices, or for an entire laboratory. It is important to note that the accredited laboratory can define its own uncertainties ranges. Accreditation therefore not always means that the uncertainty in the data is small. It does mean that the uncertainty is within the range pre-set by the laboratory and that all analytical results reported by this laboratory are within that range. Data produced by an accredited laboratory are therefore always controllable. However, non-accredited laboratories such as most academic research groups might offer more precise and/or more sensitive methods.

Accredited laboratories are often routine laboratories. Routine is also important to get an accreditation: a stable flow of analyses through a laboratory helps to build experience of the laboratory staff and will therefore improve the quality of the data. There are various reasons for laboratories to be accredited. Often, there are official and external requirements, such as for export of goods and products. The level of a contaminant should be tested and should stay under a certain maximum permissible level. This will normally only be accepted if the data come from an accredited laboratory. Commercial laboratories are normally accredited because they need to proof their compatibility to get contracts from clients.

3.1. Accreditation bodies

The International Organisation for Standardisation (ISO) plays an important role in the accreditation of laboratories. ISO is the provider of ISO protocols in which all requirements for accreditation are described in detail. Laboratories that want to become accredited need to use those ISO protocols. Accreditation bodies will check if that has been done and if so, provide the certificate of accreditation to the laboratory. Many countries have their own accreditation bodies. A few examples are the Deutsche Akkreditierungsstelle (DAkkS, Germany), the Raad voor Accreditatie (RvA, the Netherlands), the General Coordination for Accreditation CGCRE, Brazil), China National Accreditation (SOAC, WASS), and the United States Accreditation Services (USAS, USA). Accreditation bodies themselves are also under control. This is often through a membership of an international organization such as the International Laboratory Accreditation Cooperation (ILAC). The national accreditation bodies that are members of ILAC and signatories to the ILAC Mutual Recognition Arrangement (MRA) are peer evaluated under ILAC (Figure 2) (LRA MRA Signatory Search, 2023). An example of a laboratory that was accredited under ILAC on the basis of ISO17025, although not for POPs, is Analabs Limited from

Kenya. The certificate was provided by the national accreditation body Kenya Accreditation Service (KENAS), which is a member of ILAC (Analabs, 2019).



Figure 2. The roles of ILAC, national accreditation bodies, PT providers, and CRM producers in the accreditation process of laboratories.

Although good QA/QC in a laboratory also requires a budget of ca. 25-30% of the total analysis costs, many laboratories in developing countries may not have budgets allocated for this. Either with help of UNEP, GEF or donors, or without, accreditation will bring substantial costs, not only for participation in PT schemes but also for many hours of administration, all types of checks in the laboratory, calibration of balances and pipettes, use of CRMs, etc. Environmental laboratories providing data to the GMP might check with their national colleagues in food laboratories how to organize this. We interviewed two PT providers in search for possibilities for collaboration with UNEP in organizing Interlaboratory studies for POPs. In addition, a selection of stakeholders was asked to give their opinion on future developments around the quality of POPs analysis.

4. Interviews

The two PT-providers that were interviewed were the IAEA, Marine Laboratory, Monaco, and QUASIMEME, Wageningen, the Netherlands.

4.1. IAEA Marine Laboratory

The interview with IAEA took place on 17 May 2023 and was held with Dr. Philippe Bersuder and Mrs. Imma Tolosa.

IAEA has a strong focus on capacity building in developing countries. As UNEP, IAEA has a longstanding experience with working with countries all over the world. The difference with UNEP is that the IAEA Marine Laboratory is only active in the marine environment. One of the core activities is the organization of interlaboratory studies. Test materials used in those studies are often certified on the basis of the mean results of the interlaboratory studies. Such CRMs are not comparable with those produced by NIST or JRC (see 2.1), but they fulfil a useful role for the marine laboratories. The emphasis is, however, not on POPs but on trace elements, polycyclic aromatic hydrocarbons (PAHs),

and mineral oil. Interlaboratory studies for POPs are organized with a frequency of about once per 3-5 years. The last one was held in 2021.

The IAEA Marine Laboratory puts a premium on capacity building. Different from UNEP, staff members from countries can be granted a fellowship for 3-6 months at the Marine laboratory, so learn the necessary techniques for analysing POPs or other contaminants. Capacity building is also organized through the IAEA office in Vienna. New topics in which the Marine Laboratory has an interest are microplastics pollution, marine mammals and nuclear degradation. A collective organisation of an interlaboratory study on POPs would encounter some difficulties, especially as regards matrices. The expansion of the number of countries is not considered as a major problem. However, matrices such as air and human milk cannot be dealt with by IAEA. However, on the longer term a fruitful collaboration on QA/QC between the IAEA Marine Laboratory and UNEP may well be possible.

4.2. QUASIMEME

The interview with QUASIMEME took place on 23 May and was held with Dr. Wim Cofino and Mr. Steven Crum. QUASIMEME is based in Wageningen, the Netherlands as part of the WUR (Wageningen University and Research). The organization has recently merged with WEPAL/SETOC, an organization for soil interlaboratory studies, and is now called WEPAL/QUASIMEME. The activities of QUASIMEME were described under 2. They are accredited as a PT provider according to ISO guidelines. The added value of QUASIMEME is the longstanding experience with POPs interlaboratory studies. Since the beginning there was always a strong collaboration with the Vrije University Amsterdam (VU). During the interview, it appeared that QUASIMEME has an interest in organizing thePOPs interlaboratory studies for UNEP. QUASIMEME has lots of experience with producing homogeneous test materials of fish and sediment, as well as with marine water samples. They are open to consider other matrices such as passive air samples or extracts. Water, including freshwater would not be a problem. They have just accommodated a study on contaminants in freshwater for the Ministry of Transport and Public Works in the Netherlands. More difficult would be to organize interlaboratory studies on human milk. This is the domain of the Wageningen Food Safety Research institute (WFSR). However, there are ideas about collaboration and possibly creating a back office for the logistics and statistical treatment of the data and reporting, and a front office in which maybe the VU and WFSR could collaborate on the preparation of test materials. The service would not come free of charge, but cost should of course be discussed, just as frequency, and other details.

4.3. Stakeholders

Four stakeholders, two from Asia, one from GRULAC and one from Africa, were interviewed and asked for their vision on the importance of and need for quality issues in future work for the GMP. These were: Dr. Alejandra Torre, LATU, Montevideo, Uruguay, Dr. Enkhtuul Serenjav, Institute of Chemistry and Chemical Technology of the Mongolian Academy of Sciences, Ulaanbaatar, Mongolia, Dr. Teeraporn Werawutikorn, Ministry of Natural Resources and Environment, Bangkok, Thailand and Mrs. Jane Beebwa, Directorate of Government Analytical Laboratory, Ministry of Internal Affairs, Kampala, Uganda.

The following points would be proposed as common expectations on UNEP's future work towards strengthening, elevation and improvement of the national capabilities on POPs measurement and management.

The biannual interlaboratory assessment programme on POPs and especially on new POPs should continue. The programme should expand to cover a larger variety of samples in all environmental media. For the purpose of further sound management, the exploration of the development of innovative identification methods and simply screening methods (such as test kits) to facilitate Parties in identifying POPs should be accomplished in order to overcome the financial implications in developing countries.

The research and development of simplified analytical techniques for POPs analysis should be enhanced, explored, and made available, if possible, in order to facilitate the implementation of Stockholm Convention, by taking into account the socio-economic feasibility.

A knowledge hub or laboratory networking should be made available and accessible to share and exchange knowledge and experiences on sampling methods and analytical standard procedures/methods of POPs, including loads of self-learning materials (such as video clips, simply procedures, etc.).

The extraction (desorption) techniques of POPs from samples in particular POPs from products should be explored and compiled (if currently existing) or researched (if not existing) with the aim of its applicability (if feasible) as a pre-treatment step before final destruction.

There is a need for enhanced laboratory capacity and trained personnel. Environmental analysis laboratories within developing countries are often unable to provide sufficiently accurate POPs analysis. To improve laboratory capacity, it is crucial to receive training on analytical methods, instruments, and laboratory personal specializing in POPs chemical analysis. The training experts need to also impart knowledge in the area of statistical techniques for analysis of data, which is another area that is deficient in our analysts.

As different laboratories may have different capabilities and expertise, it might be unrealistic to expect all laboratories to analyze all POPs in all matrices. Adapting the assessment methods to suit the capabilities of the participating laboratories will yield more meaningful and effective results. Pursuing accreditation for multiple types of POPs and matrices might be too ambitious at this stage. Accreditation for specificPOPs analysis is a more realistic goal. Support from UNEP or other related organizations to realize laboratory accreditation is needed.

Implementing the ISO/IEC 17025:2017 standards requires continuous improvement and compliance and thus staff needs to have their analytical skills enhanced and technical competence continuously checked.

5. Discussion

Within UNEP is a clear wish to encourage accreditation of laboratories in countries that deliver information to the GMP. Most of the developing countries, however, struggle to obtain the right level of quality which is needed to become accredited. More in detail, it does not make sense to become accredited for an analytical method for e.g., DDT, if the precision the laboratory can guarantee is $\pm 50\%$ or more. Therefore, first, investments should focus on getting at least a selected number of laboratories on the right quality level.

It is likely that various laboratories in developing countries seriously underestimated the efforts needed for accreditation. Accreditation is sometimes more seen as 'a solution for all problems', while the problems need first to be solved before an accreditation can be provided.

The capacity building activities of UNEP during the last decade, with a focus on a relatively short onsite training, have not resulted in the desired result. The recent interlaboratory studies on POPs underline the lack of quality in many laboratories. The model, as used by IAEA, to offer fellowships for 3-6 months may be a better alternative for such a training of staff. During the recent UNEP training programme, Mr. B. Santiago Avila from the University of Antioquia, Medellín, Colombia stayed for half a year at the CSIC, Spain for aPOPs training. Experiences of the CSIC staff and the trainee were very positive. Apart from the training itself, the bond between the laboratories created in this way, is an added value. However, no sufficient quality can be achieved if the laboratories do not work onPOPs analysis on a regular basis, with a continuous workflow through the laboratory.

Food laboratories in developing countries have shown to function much better, thanks to their continuous workload. It may be advised to liaise with the Food and Agriculture Organization of the United Nations (FAO) to see if collaboration, or even copying of their way of working would be useful. FAO ensures that laboratory staff have the knowledge and skills required to correctly carry out their functions. Support may be provided to obtain international accreditation. FAO training events are often designed to encourage networking with national universities, research centers, regional or international laboratories. This helps to create informal networks, which can help laboratory staff meet ongoing challenges and in supporting further staff development (FAO, 2023). Although many analyses for food safety purposes are easier than analyses of POPs, it seems worthwhile to check with FAO where similarities can be found and where cross-fertilization can take place.

The element of providing support to obtain international accreditation might sound attractive for UNEP. Even more important is this strategy: FAO sensitizes policy makers on the role of laboratories and promotes a long-term vision considering analytical needs and existing national capacities and resources. This is exactly what is until now missing in the UNEP approach. National authorities and policy makers are not sufficiently enough aware of the urgency of POPs analyses, and the consequence of ratification of the Stockholm Convention. If they were, they would support regular sampling and analysis programmes on POPs. Other interesting elements in FAO's approach are the encouragement of collaboration with universities and encouragement of (informal) networking. An example of networking of Interamerican food laboratories can be found on the website of Inter-American Network of Food Analysis Laboratories (INFAL) (INFAL, 2023). Collaboration and networking of food laboratories also takes place - and is encouraged by FAO - within the Codex Committee on Methods and Sampling (Codex, 2023).

From these various options, it seems that the food laboratory world is better organized than the world of environmental laboratories. This is probably due to history - food laboratories are much older whereas environmental laboratory works only started in the beginning of the 1970s - and due to the (supposed) higher importance of ensuring food safety, and due to economical/legal reason (food export). It seems a good idea to study where UNEP can learn from FAO/Codex Alimentarius or strive for collaboration with FAO. It should, however, be emphasized that the complexity of the POPs analysis may cause a bigger challenge for UNEP than the relatively easier food analyses cause for FAO. The interviews with the stakeholders all emphasize the need for continuation of the interlaboratory studies. Some even ask for an extension of the selection of test materials offered to the participants. This is remarkable, because during the last four studies many laboratories only analyzed one or two, maybe three of the offered test materials and left a large number of test materials unused, as well as a number of POPs not analyzed. In general, the stakeholders interviewed ask for more possibilities in training, video support, and method development support, sometimes for more matrices and more compounds. This sometimes goes beyond the aims and scope of the GMP, because the core matrices are air, water and human milk and the compounds are limited to POPs. This shows the needs of these laboratories, which most likely cannot be solved by UNEP or GEF but need to be addressed by the authorities in their own countries.

It seems necessary for UNEP to explain again what is expected from the countries and what can be expected from UNEP. Currently, many countries expect a sort of full support in the development of their environmental laboratories, while UNEP can only assist in them in carrying out their tasks that follow from their ratification of the Stockholm Convention. Something UNEP/GEF and donors could do, is trying to facilitate better support and service for mass spectrometric instruments (de Boer, 2023). In any case, there is a broad agreement on the need for continuation of the interlaboratory tests, to improve the ability of the staff to analyse POPs and to underpin a possible accreditation. Expansion to more matrices, if not only for economic reasons, is not recommended. The interviews with the two PT providers, QUASIMEME and IAEA offers options for further contact and possible collaboration. Finally, it is clear that accreditation bodies do not provide proficiency tests or interlaboratory studies. Accreditation of a laboratory can be obtained, but only after a serious investment in manpower, probably for at least 2 or 3 years. Very few laboratories in developing countries are currently able to realize that on their own.

6. Conclusions and recommendations

There are clearly several lessons to learn from the UNEP capacity building projects during the last decade. In that sense those projects have been very useful. Very briefly, training of staff was too limited in time and too superficial, costs of the interlaboratory studies were too high, while the results were disappointing, and did not assist the laboratories to get accredited. From the paragraphs above a series of recommendations emerges.

Training of laboratory staff

One or two laboratories per region should be selected to be extensively trained inPOPs analysis. A model used by the IAEA with grants for training in an expert laboratory for half a year in an expert laboratory (see also the aforementioned example of the training of a Colombian staff member by CSIC) is strongly recommended. In a second stage, the training should be taken to a next level, so that the trained centers will be able to provide training to otherPOPs laboratories in the region.

Accreditation

Once at this level, these laboratories, if they want, could also be accredited, provided there is a regular workflow of POPs analyses through the laboratory. Another condition for accreditation is the presence of or investment in, possibly by donors, good quality mass spectrometers, both GC/MS and LC/MS, together with (what is entirely missing now) the availability of service of those instruments and ¹³C labeled internal standards (see recent report on optimized monitoring (de Boer, 2023)).

Interlaboratory studies

Ongoing interlaboratory studies on POPs are essential for all laboratories working on POPs. The frequency can be debated but should preferably be once per two or three years. The size of these exercises should be trimmed compared to the previous series of four UNEP interlaboratory studies. This can be done in the following way.

<u>Matrices</u>: Use only core matrices air, water and human milk. Leave out sediment, fish, unknown solutions, human blood and transformer oil.

<u>Selection of POPs</u>: Recent monitoring results show that many POPs have worldwide declined under detection limits. With that the need for intercalibration has recidivated. Some of the more recently added POPs are, obviously, more relevant. The new interlaboratory studies should therefore include: six indicator PCBs (28, 52, 101, 138, 153, 180), PBDEs (47, 99, 209), α , β and γ -HBCD, PFAS (EFSA set, PFOS, PFOA, PFHxS, PFNA), short and medium-chain chlorinated paraffines (SCCPs and MCCPs),

dechloranePlus, lindane (γ -HCH), trans-chlordane, HCB, PeCB, HCBD, and α -endosulfan. All other POPs, including HxBB, toxaphene, mirex, dieldrin, endrin, aldrin, all other chlordanes, β -endosulfan, endosulfan suphate, heptachlor, cis and trans-heptachlor epoxide, chlorinated dibenzodioxins and dibenzofurans, and chlordecone can be left out because at most locations, concentrations have dropped to insignificant values.

Frequency: Once per three years.

<u>Selection of laboratories</u>: It should be checked if the invited laboratories are the best and also the most relevant laboratories that will contribute to the UNEP/GEF GMP projects. If not, a full price should be asked for participation, as was already done in the previous studies for laboratories from OECD countries.

Collaboration

Joining forces with either the IAEA in Vienna or with FAO can be very beneficial for training of laboratory staff. Due to their accreditation for running interlaboratory exercises and their statistical experience, QUASIMEME could be useful partner for running the interlaboratory studies, in collaboration with universities or other partners. Alternatively, IAEA could be useful in collaboration with UNEP.

7. Reference

- Analabs (2019). https://kenas.go.ke/cabs/entry/analabs-limited/
- Codex (2023). https://www.fao.org/fao-whocodexalimentarius/committees/committee/en/?committee=CCMAS
- N. Bruun Bremnes, L. Småstuen Haug, C. Thomsen (2021). Interlaboratory Comparison on POPs in Food 2020 The twenty-first round of an international study. www.fhi.no/ILC. Norwegian Institute of Public Health, Division for Infection Control and Environmental Health, Department of Environmental Health, Section of Environmental Exposure and Epidemiology, Oslo, Norway.
- J. de Boer (2023). Towards optimizedPOPs monitoring in developing countries to support the effectiveness evaluation of the Stockholm Convention. Draft report for UNEP, 10 March.
- EPTIS (2023). https://www.eptis.bam.de/eptis/WebSearch/main?lastSearchTerm=%22PT+provider+ID%22%3A 119332&searchTerm=%22PT+provider+ID%22%3A119332&newSearch=newSearch&facetFieldCl assifications=analytical+chemistry
- EU (2017). Regulation (EU) 2017/625 of the European Parliament and of the Council, European Union, Brussels, Belgium.
- EURL (2023). https://eurl-pops.eu/user/pages/05.news/06.technical-guidance-for-pts-v1-2/Technical%20instructions%20EURL%20POPs%20PTs%20v1.2_web.pdf?g-ddf3b8b8
- FAO (2023). https://www.fao.org/food-safety/food-control-systems/official-controls/laboratorydevelopment/en/
- FAPAS (2023). https://fapas.com/shop/search?producttypes=1
- H. Fiedler, I. van der Veen, J. de Boer (2022). Assessment of four rounds of interlaboratory tests within the UNEP-coordinated POPs projects. Chemosphere 288, 132441.
- IAEA (2022). Worldwide interlaboratory comparison on the determination of organochlorine compounds, polybrominated diphenyl ethers and polycyclic aromatic hydrocarbons in a fish sample. Report ILC-IAEA-ME IAEA/AQ/66, ISSN 2074–7659, SL-2019-01-OC. International Atomic Energy Agency, Vienna, Austria.
- INFAL (2023). https://www.rilaa.net/en/quienes-somos

- K. Krätschmer, A. Schächtele (2019). Interlaboratory studies on chlorinated paraffins: Evaluation of different methods for food matrices. Chemosphere 234, 252-259
- LRA MRA Signatory Search (2023). https://ilac.org/signatory-search/

Part 2: Towards optimizedPOPs monitoring in developing countries to support the effectiveness evaluation of the Stockholm Convention

1. Introduction

The Stockholm Convention (SC) on persistent organic pollutants (POPs) is a legally binding instrument for the protection of human health and the environment and enforced by the United Nations (UN) on a global level. The objective of the SC on POPs is to protect human health and the environment from POPs (UNEP, 2019a). POPs are identified based on their persistence, bioaccumulation potential, toxicity (adverse effects) and mobility (potential for long-range transport). Once identified, they are listed in Annexes A, B and/or C, sometimes time with limited exemptions. What follows are actions by the member states to eliminate these chemicals worldwide by either prohibiting, eliminate or restricts their production and use. The SC was adopted in 2001 and entered into force in 2004. It started with 12 POPs, but currently, there are 34 POPs. None of the initial 12 POPs have successfully been phased out completely, although bans on production and use have been established. The global monitoring plan (GMP) under the SC was designed to assess the effectiveness of the SC in globally reducing POPs. In other words, it is meant to monitor if, and to which extent measures on reduction and restriction on the production, storage, and usage of POPs would result in lower concentrations in the environment. Four core matrices were selected by the conference of the parties of the Stockholm Convention for monitoring: air, human milk, human blood, and water. Almost 20 years after the start of the SC activities, results of monitoring programmes have become available, especially for the human milk and air monitoring programmes.

From 2016-2023, UNEP, in collaboration with the Secretariat of the Basel, Rotterdam and Stockholm (BRS) Conventions, and with financial support provided by the Global Environment Facility (GEF), implemented four regional projects to support the GMP for POPs in forty-two countries in the regions of Africa, Asia, Pacific islands, and Latin America and the Caribbean (GRULAC), including, in collaboration with the World Health Organization (WHO), a global survey to generate data on concentrations in human breast milk of the POPs listed in the SC.

The objective of this report is to learn lessons from these recent UNEP/GEF POPs GMP projects to see where improvements in terms of quality and cost-effectiveness can be installed prior to a new round of monitoring. First, a comparison will be made with other monitoring programmes. After formulating the key parameters, options for a new program will be discussed, and recommendations will be given. Attention will also be paid to aspects of national interest in developing countries.

2. Comparison with other monitoring programmes and the needs of developing countries

2.1. Other monitoring programmes on POPs

Monitoring of POPs is not only done by the UNEP/GEF POPs GMP projects. Worldwide, there are numerous projects, networks or initiatives in which POPs are being monitored to establish spatial and temporal trends, sometimes along with the monitoring of other contaminants such as trace metals. Many of these programmes are not related to the SC and the data produced by those programmes are not always included in the data warehouse of the SC.

The European Water Framework Directive is for example a programme in which every six years river basin management plans are reported (WFD 2023). The objective is to achieve a good status in all bodies of surface water and groundwater by 2027. The compartments involved are groundwater and surface water, and the assessments comprise ecological status (surface water only), chemical status (groundwater and surface water) and quantitative status (groundwater only). The chemical status of surface water is assessed against standards for priority substances listed in the Environmental Quality Standards Directive. These standards are set to protect the most sensitive aquatic species, as well as humans who can be affected by secondary poisoning. Linked to the WFD is the Marine Water Strategy Framework Directive (MSFD). This is European legislation, focused on European marine waters, with also the aim to obtain a good environmental status of the marine waters (MSFD, 2023). Both frameworks have in common with the SC GMP that they strive for improvement of the environmental quality and have set dates to reach their goals. The WFD and MSFD comprise more chemicals but do include POPs. Older data on the European marine waters have been collected by the Olso and Paris Commissions (OSPARCOM) in collaboration with the International Council for Exploration of the Sea (ICES). OSPARCOM is supported by the governments of Belgium, Denmark, Finland, France, Germany, Iceland, Ireland, Luxembourg, The Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, United Kingdom, and the EU (OSPARCOM, 2023).

Another interesting monitoring programme is the Partnership for the Risk Assessment of Chemicals (PARC) (Norén, 2023). PARC builds on the experiences of HBM4EU (Human Biomonitoring for Europe) (Ougier et al., 2021). Both programmes focus on human monitoring, mainly in various body fluids, including urine and serum. HBM4EU was launched in 2016 with the aim of improving the collective understanding of human exposure to hazardous chemicals and developing human biomonitoring as an exposure assessment method. The project included 120 partners from 28 participating countries – 24 EU member states plus Norway, Switzerland, Iceland, and Israel, and the European Environment Agency. It ended in June 2022 and was replaced by PARC. PARC encompasses all aspects of chemical risk assessment, in particular aiming at better anticipating emerging risks, better account for combined risks, and underpin the concrete implementation of new orientations in European public policies to safeguard health and the environment in response to important issues for health, the ecology, and citizens' expectations. So, PARC is much broader than justPOPs monitoring. However, exchange of information on POPs might be an interesting option for UNEP/GEF to explore.

Four global or regional programmes that include air monitoring of POPs and submit data to the SC GMP are the Arctic Monitoring and Assessment Programme (AMAP), the Global Atmospheric Passive Sampling Network (GAPS), the POPsEA (Environmental Persistent Organic Pollutants Monitoring Project in East Asian Countries) project and the Monitoring Network (MONET).

AMAP aims to provide reliable and sufficient information on the status of, and threats to, the Arctic environment, and scientific advice on actions to be taken in order to support Arctic governments in their efforts to take remedial and preventive actions relating to contaminants and adverse effects of climate change (Hung et al., 2010). POPs are an important group of contaminants in AMAP, but other contaminants are also included.

The GAPS program is part of a sampling network with approximately 65 sites on seven continents that was established to investigate air concentrations of POPs (Schuster et al., 2021). The results of GAPS are used to assess time trends of POPs concentrations in air and to develop and test global atmospheric transport models for POPs. This information is being compiled to assess the effectiveness of recent control measures on POPs that have been established as part of the international treaties on POPs such as the SC. AQUA-GAPS was set up in 2017 as a global monitoring network to determine the presence of toxic chemicals in aquatic environments and gain insight on their geographic distribution as well as temporal trends (Lohmann et al., 2017). The network supports the SC by generating data on PFOS (perfluorooctanesulfonic acid).

The objective of the POPsEA programme is to build POPs monitoring capacity in the East Asia region and to compile the monitored data and background sites to contribute the GMP for the SC and the effectiveness evaluation (POPsEA, 2023). It was mainly set up because there are many South-Asian countries that lack sufficient funds, advanced technology, knowledge, or personnel to develop a solid national and regional POPs monitoring program. The POPsEA programme's core media is air, and it has set up active and passive air samplers in each of the participating country. The Programme's capacity building component has donated active air samplers and consumables to participating countries, and organized technology transfer for sample collection.

MONET was established in 2003 in the Czech Republic. It comprises more than 450 sampling stations in 44 countries, on three continents – Europe, Africa, and Asia, on which monitoring of POPs in air is being carried out. In Africa the MONET network include 9 countries (White et al., 2021). Data are provided to the SC GMP data warehouse (GMP, 2023).

Together, on a regular basis, these four programmes deliver a large set of data to the GMP data warehouse. GRULAC region and the Pacific are not completely covered by these four programmes, including also coverage gaps in southern Africa and Asia. All data are stored in the data warehouse. These programmes are not under control by UNEP. That means that costs are relatively low as there is no payment requested for the POPs analyses, but also that changes in the strategies of these programmes could imply a sudden strong reduction of the data input in the GMP data warehouse. The recent GMP programme contained a so-called national samples project. Countries were invited to select samples for POPs analysis which they found most important. They were only asked to include one fish sample in the ca. ten samples that they could send to the reference laboratory (and also analyse them in their own laboratories). The results are still under study. An array of different matrices, including fish, shellfish, sediment, eggs, butter, chicken, cow milk, mutton, horse meat, beef, raw sugar, honey, maize, bananas, and others was sent to the reference laboratories for analysis. However, in general countries had difficulties to select suitable samples. The emphasis was on products for human consumption, which can be linked to a high interest in food in the participating developing countries and to export interests. The project did not deliver a common matrix that could serve for all locations, although fish and sediment were dominant. Chicken eggs could be an option. They are available worldwide. The existing POPs can relatively easily be detected in eggs, and it is an excellent matrix for PFAS, which bind to proteins (Göckener et al., 2020). Maybe the feed or local sources could be a disturbing factor. Eggs from battery cage chickens should of course be avoided. Obviously, there is an overlap with the work of national food laboratories. In almost all developing countries, food safety has a priority compared to environmental research. It may, therefore, be questioned if UNEP should also include food items as a matrix in the POPs monitoring. Collaboration with the Food and Agriculture Organization of the United Nations (FAO) might be interesting and possibly cost-effective. Another matrix that may be of interest for countries isPOPs waste. Old stockpiles, dump sites, and transformer oil waste still need to be cleaned and removed. Analyses need to be carried out to check how successful the cleaning operations have been. Such matrices normally contain high levels of POPs. They may easily contaminate the instruments used and disturb the POPs analysis in other matrices that occur on a micro-level. Nevertheless, it might be necessary to consider programmes for such matrices. Finally, some POPs, such as the polybrominated diphenylethers (PBDEs) might be present in electric and electronic waste that may be dismantled in developing countries. Training programmes on POPs analysis in these matrices also seem useful.

No doubt, there are morePOPs monitoring programmes in addition to the aforementioned ones. Most of those will address only a specific region such as e.g., Antarctica (Kallenborn et al., 2013) or a specific country. Few will comprise the entire globe.

2.2. The role and needs of developing countries

A global monitoring programme should obviously be representative for the entire world. That implies that samples of a certain preferred and common matrix should be taken from each continent and preferably from more than one location per continent. The UNEP/GEF GMP projects had a focus on developing countries. Most of the sampling sites in the air monitoring programme laid between 36 °N and 36 °S (De Boer et al., 2023). The aim of this report is to evaluate the role of developing countries and to recommend on optimization of monitoring in those countries. It is, however, essential to distinguish between optimal global POPs monitoring and monitoring of POPs in developing countries. At this moment, these two elements cannot and should not be combined in one unified monitoring programme because the analytical capability of the laboratories in developing countries is insufficient. As it is now, continued and further optimized use of data from the MONET and GAPS programmes should be used for globalPOPs trend monitoring. This does not mean that these programmes should not undergo a critical evaluation and further optimization. No doubt, there is room for improvement. Currently, there is for example no check on the quality of the analyses in the expert laboratories. Data from CRM analyses and interlaboratory studies should be provided. In fact, the MONET and GAPS programme work as the human milk monitoring programme does. Samples are collected by local in the various countries and sent to reference laboratories which carry out the chemical analyses. Including developing countries in the global POPs monitoring with a full-grown role, which entails much more than only taking samples, requires substantial investments.

At the start of the UNEP/GEF GMP projects, long discussions were held about the role of developing countries. It was agreed that capacity building should be part of the projects work. Indeed, throughout the last decade efforts have been made by UNEP/GEF to build capacity in many developing countries. The corner stones of that capacity building were two programmes: regular interlaboratory studies (ILS) on POPs and on-site training in POPs analysis. In addition, workshops on POPs analysis were held in reference laboratories, standard operating procedures on POPs analysis were prepared and made available, personal guidance was given by experts, and other activities, all focusing on improving the ability of the countries to analyse POPs, were carried out.

The ILS were important in showing the ability of the participating laboratories in analyzing POPs (Fiedler et al., 2022). The ILS attracted a lot of laboratories. With more than 100 laboratories participating in each of the four rounds, this was the biggest ILS on POPs ever organized. ILS are the only blind tool, and give, as such, the best picture of the quality of a laboratory. In all four rounds advice on what to do and what not to do was given to the participants. It was hoped that an improvement in the ability of laboratories in analyzing POPs could be shown. Unfortunately, the progress was less than was hoped for. Some laboratories did make progress, but many did not.

Training in POPs analyses to a large number of laboratories in Latin-America, Africa and Asia was given on-site (Leslie et al., 2013). The training consisted of a theoretical and a practical part. The advantage was that the staff learned to carry out thePOPs analyses in their own laboratory. Staff of expert laboratories was available on the spot for ca. 10 days per training. Unfortunately, the training was much less effective than was expected. Independent of the continent, there were a number of common causes. i) The laboratories had to function under poor to very poor conditions, which did not fulfil the requirements for a proper POPs laboratory. For example, air conditioning was often lacking, so solvents evaporated easily, windows were open and attracted a lot of dust in the laboratories with on the dust interferences or POPs themselves, electricity failed from time to time, fume hoods were not or only partially working, glassware was inadequate, instrumentation was not functioning or dirty, etc. UNEP/GEF installed a procurement scheme in which laboratories could ask for analytical reference standards, glass ware, septa, liners, chromatography columns and other consumables but although these materials helped at the time of the training, they did not offer a

permanent solution. Laboratory staff had great difficulties to order consumables and get service for their instruments when broken. Due to bureaucracy and complicated rules for ordering abroad, and sometimes due to lack of funding, time needed to deliver goods or service easily mounted up to half a year or more. In such a way a laboratory cannot function. ii) Basic knowledge of (analytical) chemistry was often lacking. Staff present at the training was therefore often not able to understand the ins and outs of the complicated POPs analysis. In some cases, staff present at the training had no chemistry background at all. iii) In some cases, staff with sufficient background and talent, appeared to leave the laboratory after the training because their 'market value' was raised and they found a better-paid job. iv) It appeared that the management of the laboratories was unable to fund regular work on POPs in the laboratory.

POPs analyses are complicated and can only be carried out properly when done on a regular basis. It can be compared to using a computer program. If not using that regularly, one forgets details easily. The lack of funding – and interest – finds its base of course with authorities. Despite having signed the SC, the responsibility to analyse POPs in their country is lacking, presumably because other issues like shortage of food and health problems are more important. It became very clear that continuing the support in the same way does not make sense. Interestingly, there are commercial laboratories in developing countries that do function, also for POPs analysis. One such laboratory was visited by experts during a training in Uganda. It showed that is not impossible to do POPs analysis in developing countries. However, there must be a strong incentive to install a well-functioning laboratory, maintain it properly, and guarantee a continuous flow of samples though the laboratory. That incentive is lacking from almost all authorities responsible for the POPs laboratories in developing countries. Of course, there are a few better performing laboratories, but not more than one or two per continent. So, whereas the projects had presumed that with a two-weeks training and a procurement programme most laboratories could be enabled to carry out the POPs analyses themselves, in practice the reasons for not functioning laboratories were much more profound. The gap in quality of POPs laboratories between the developing countries and the develop countries is much bigger than anticipated.

3. Key factors for optimal POPs monitoring in developing countries

There are two essential conditions to be fulfilled to enable good quality POPs monitoring in and by developing countries. Each of them will be discussed below. Failure to install and guarantee these two conditions will imply that all other actions to improve the capacity for POPs monitoring in developing countries will be in vain.

3.1. Responsibilities and commitment of authorities

POP monitoring can only be carried out when done on a regular basis. That means that analysts in the laboratory should only have the task to carry out those analyses with no other tasks to distract them. Developing countries have shown a high interest in receiving training. That training should, however, only be given after agreeing on a firm contract with the responsible authorities that guarantees a well-functioning laboratory for the coming decade at least. In other words, donations and investments by UNEP/GEF should only be made when the countries pay back with dedication, not only on paper but in practice and with a very clear and firm commitment. This part has been much too weak in the past. This is the first and most important condition. Without meeting this, capacity building is useless.

3.2. Equipment

A second important issue is the availability and functioning of equipment for POPs analysis. At the start of the SC, many laboratories worldwide, also in the western world analysed polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) by gas chromatography (GC) with an electron capture detector (ECD). Only for dioxin analyses a mass spectrometer (MS) was applied. Nowadays, every self-respecting POPs laboratory analyses POPs by GC/MS. Moreover, liquid chromatography with MS (LC/MS) is available in most laboratories to analyse PFAS. The use of MS has replaced the use of ECD because i) MS instruments have become cheaper (although still quite expensive (ca. 100-200 k\$) for developing countries), ii) due to lower environmental concentrations especially OCPs cannot be properly determined because interferences have become dominant in chromatograms, iii) the accuracy and linearity of MS instruments is much better than that of ECD, iv) through the development of clever software, MS instruments have become easier to use. A few developing countries do have a mass spectrometer (GC/MS) in their laboratories, often through a very kind gift of donors. However, in most cases the instrument is not functioning, while service is not available.

Throughout the last decade the lack of proper GC/MS (and LC/MS) in developing countries was discussed at workshops and evaluations of the GMP results. That situation was taken as a fact, and never in these discussions a solution was brought forward. Trying to set up a good quality POPs laboratory without GC/MS and LC/MS will be a waste of money. The ECD will vanish from laboratories as far as it has not done so already during recent years. Therefore, a plan should be developed to bring MS into laboratories of developing countries. Only then, they could take over tasks from reference laboratories and carry out the POPs analyses themselves. If, for example, only one or two donor countries would, instead of donating an instrument, donate the costs for maintenance and service, the problem could probably be solved. MS companies are willing to offer service but not when only one or two MS instruments are present on a continent. That is too little to host an engineer in a nearby office. A meeting between MS companies, donors and UN representatives should be able to discuss and solve this issue. At least it is worth trying. This condition needs to be fulfilled to build sufficient analytical capacity for POPs in the developing countries. It is expected that the list of POPs will grow. The UN Global Chemical Outlook II predicted a doubling of the chemicals global market between 2018 and 2030 (UNEP, 2019). Those chemicals will not only be safe chemicals but will probably also include future POPs. Some of the new POPs might have a more polar or mixed character, as we have seen with the PFAS. That has consequences for the analysis. Therefore, not only GC/MS but also LC/MS instrumentation will appear to be essential for POPs analysis in the coming decades.

3.3. Costs

Until now, monitoring activities in developing countries have costed huge amounts of funding. It is justified to ask if costs could be reduced without compromising the results. There are certainly a few options to reduce costs. These can be found in i) reducing the number of sampling locations, ii) reducing the frequency of sampling, iii) reducing the number of POPs, iv) use of models.

To get a proper impression of temporal global trends inPOPs concentrations, there is no need to sample on 43 locations as was done during the recent sampling campaign. First, there are data from the other programs, MONET, AMAP, GAPS. Secondly, if properly designed and distributed equally over the globe, ca. 18 locations could do the job. Details are given in 4.4. The costs are not exactly halved by this change because, to reduce the variation in the results, improvements in the programme are required, such as duplication of samples and use of internal standards (see 4.2.1). However, further savings can be obtained by reducing the frequency of sampling and analysis. From previous data and from the literature, it appears that some POPs, e.g., the PCDDs and PCDFs are continuously decreasing and arrived already on rather low levels. It will be sufficient to analyse these compounds only once per ca. ten years, and only on even a smaller set of locations (see 4.4). Because more POPs

are decreasing in concentration, and/or cannot be detected at all on most locations, the total number of POPs can be reduced, probably from 34 down to 18 POPs. In addition, for some of the mixtures, not all congeners or isomers need to be analysed (see 4.3). In this way, substantial reductions in costs can be achieved while the quality and reliability of data will be improved. The smaller number of POPs will also cause a cost reduction in the ILS. Finally, there may be a possible reduction in costs by using models. This, however, is not an option for the short term. Models need to be fed by lots of data and there are uncertain factors such as decisions to terminate production of certain POPs or not, which cannot be predicted by models. A study on how to work with production figures is recommended. This would also shed more light on the importance of limiting production of POPs, which is, obviously, one of the goals of the SC.

4. Building a new monitoring programme

With the existing programmes organized from developed countries (AMAP, MONET, GAPS) delivering data to the GMP data warehouse, the question is relevant if there is a need for an additional programme. The answer would be yes, if UNEP/GEF would like to guarantee data input for the coming decades and to continue filling geographic data gaps in several UN regions. A second reason, not less important, is the desire to invest in analytical capability in laboratories in developing countries. For the moment, it seems likely that GAPS, AMAP, and MONET will continue to deliverPOPs monitoring data to the GMP. AQUAGAPS is still a junior programme and should be compared to the alternative of point sampling, which should preferably take place in lakes and not in rivers. The success of the UNEP/GEF/WHO human milk programme, and of the monitoring carried out by GAPS and MONET is based on the analyses that are all being carried out in one centralized laboratory. Continuing with GAPS, AMAP, and MONET only will therefore mean that development of analytical capability in developing countries will come to a compete standstill. Assuming this would be an undesired development, below a possible structure is suggested in which capacity building for POPs analysis will be the most important component. It will also address cost-effectiveness of a possible continued monitoring program.

First of all, the two key factors for success, as described in Chapter 3, should be established. Without a full commitment of the participating countries – which should be much more than was observed until now – and a solid plan for installing working GC/MS and LC/MS instrumentation, capacity building would be useless. Although the MS instruments are needed in various countries, we start here from the idea that one or two laboratories per region/continent will be selected for capacity building leading to an independent reliable high qualityPOPs data production, comparable to that of the reference laboratories. These selected laboratories should, once successful, get a role of referencePOPs laboratory for their region, where other laboratories from the same continent can be trained in future. There are of course different ways to select the candidate laboratories. Based on the results in the four UNEP/GEF ILS rounds, it could be checked if and how much progress was made. Unfortunately, there are very few that made consistent progress. Impressions from the recent capacity building programmes could also be used. One or two laboratories were indeed better performing, but all were still relatively far from the desired quality. If possible, it might be good to look also for laboratories that, until now, did not participate in the ILS or in the recent capacity building projects, such as, e.g., in South-Africa and India. For the Pacific, the only available laboratory in Fiji is not likely to qualify for this central role, as little progress, and a decreasing interest in GMP work has recently been noticed. Possibly, Indonesia could take over that role. Giving such a responsibility to Australia would obviously not be a solution for capacity building. Clearly, it will not be easy to go this way, as strong commitments from the candidate laboratories are requested, and moreover from the authorities involved are requested. Assuming this could be achieved, a training program could include the following items.

- Selection of one or two laboratories per region/continent
- Make firm agreements for the coming ten years with the responsible authorities and make sure payment will be terminated in case of no show
- Ensure GC/MS and, if possible, LC/MS, *including service/maintenance* are present in the selected laboratories
- Training of one or preferably two scientists from the candidate laboratories in a reference laboratory in Europe, the US or Japan, for at least half a year, including GC/MS and LC/MS training
- Following or already during that training, exchange of samples and comparison of analytical results
- Participation in the ILS (see below)
- A one or two-weeks hands-on workshop in one of the reference laboratories where laboratory staff of all selected laboratories meet and discuss analytical issues to i) improve their knowledge and ii) create and strengthen a mutual bond that will make exchange of problems and mutual consultation much easier
- If possible, training towards the achievement of accreditation for POPs analysis (if not already the case). This will be discussed in a separate report
- During this training period of ca. 1 1.5 year, it would be helpful if air sampling stations in the countries of the selected laboratories would be available. Data produced could be added to the GMP data warehouse. In total, this would comprise not more than six laboratories in six different countries.

4.1. The interlaboratory studies

The last four UNEP/GEF ILS on POPs have all been received with great enthusiasm (UNEP, 2023). That can be seen from the high participation degrees and from the various positive responses from participating laboratories and organizers (Fiedler et al., 2022). It is a blind test for laboratories, and accreditation bodies require participation in such tests. The four recent ILS studies were not only huge in number of participants but also in their offer of matrices. Apart from an air extract and human milk, the ILS studies also offered fish, sediment and in some cases water, transformer oil and human serum as test materials. The substantial workload, also caused by the growing number of POPs, deterred many participants which made that some, although having registered, did not participate at all, and many participated but only for one or two matrices. Considering, in addition, the costs of these exercises, the advice is reducing the number of matrices to only an air extract and human milk, and possibly a water sample for PFAS. Fish, sediment, and the standard solutions as well as human serum should be taken out, because results of such exercises do not directly contribute to the GMP in which the core matrices are air, human milk and water (only for PFAS). Fish and sediment are often included in other interlaboratory schemes such as those organized by QUASIMEME or WEPAL (Wells and de Boer, 2006). If laboratories have an interest, they can participate at their expenses. There are sometimes reduced fees for developing countries. The proposed cut-back ILS could be held every other year. A lower frequency would create a too long gap without proper tests for the participants. In this way costs would be cut back by more than 50%.

4.2. Matrices

One of the major challenges of a global monitoring programme is to select a proper matrix of national interest in which POPs can be analyzed. Within one country or a specific region, it is easier to select a representative matrix. POPs are bioaccumulating compounds. That means they occur in elevated concentrations in organisms, such as fish. Selecting a specific fish species can generally be

done within one country or region. There are good examples, e.g., of almost 50 years monitoring of POPs in eel (*Anguilla Anguilla*) in the Netherlands (De Boer et al., 2006), and a similar programme, although somewhat shorter, in Belgium (Belpaire et al., 2009). But even a selection of a proper 'bioindicator' in one country has challenges. The fish should not migrate too much, fishes should have similar lengths/weights, should male or female fishes be used or both? The spawning period should be avoided, because in that period the fat content varies substantially. Eel is ideal because it only spawns at the end of its life. It is also a non-migratory fish for ca. 15 years, until it starts to travel back to its spawning grounds. It is a fatty fish, which facilitates the determination of POPs and the fats in the eel are mainly triglycerides which are relatively easy to handle in the clean-up prior to analysis (de Boer and Hagel, 1994). For other fishes this is all more challenging.

Broadening the area to the entire globe implies that one fish species is not available on each site worldwide, let alone that that species would also show the ideal properties to serve as a bioindicator. With the unavailability of a suitable fish species as bioindicator, the most suitable matrix for POPs monitoring is not available for worldwide monitoring. Many discussions were spent at the start of the GMP on selecting the best alternative. At the end air, human milk and, for some specific purposes, human blood were selected. Water was added later to serve for monitoring of per- and polyfluorinated alkyl substances (PFAS). Human milk has the obvious advantages of monitoring in humans, a high fat content, a fine definition (milk of primiparous mothers, sampled within the first three months after birth), and global availability. A database on POPs in human milk was already set up by the World Health Organization (WHO) (Malisch et al., 2010). We will not further discuss human milk monitoring, as there is little discussion on the continuation of this useful programme.

4.2.1.Air

Air was obviously selected for POPs monitoring in the first place for its global availability.POPs concentrations in air are low, but by concentration in passive samplers over periods of months, or by active monitoring during hours/days, those concentrations can be elevated to enable a proper detection. In addition, air is relatively clean, and clean-up of air samples can be very successful, resulting in relatively clean chromatograms. The challenge of POPs monitoring in air is, however, in the sampling phase (de Boer et al., 2023). Passive samplers with polyurethane foams (PUFs) need to be hanged out for ca. three months for most POPs. This may already need a compromise because same of the more volatile POPs such as penta- and hexachlorobenzene, PFAS, and others may reach equilibrium sooner than three months, after which temperatures may start to influence the data too much. Also, by adding more POPs to the existing lists, in particular those with a more polar character such as several PFAS and pentachlorophenol, may require addition of specific carriers to the PUFs, which is not needed for non-polar POPs. The highest concern is, however, in the relatively large uncertainty of the data produced. Due to varying temperatures and wind speed, during a threemonth period different volumes of POPs may be accumulated. This is true for the same location in different seasons and for different locations in one season. Temperature differences around the world can be huge. It is also not easy to correct for temperature: when should those temperatures be measured? Once per day or night, and will the average be taken or the median? The GAPS and MONET programmes use a model for translating the POPs concentration per PUF to a concentration of the POPs in air. Whether or not corrected, uncertainties in the POPs concentrations in air measured by passive sampling amount up to 50% or more (Wania and Shunthirasingham, 2020, Melymuk et al., 2021). In addition, there is an analytical error that is generally around 25% for a properly optimized and validatedPOPs method. However, close to the detection limit, that uncertainty can creep up to 100%. Altogether, this makes air monitoring quite a rough tool for assessing a change in temporal trends inPOPs concentrations worldwide are decreasing. Only very substantial decreases would maybe be observed.

At a first glance active sampling is more precise (Lazarov et al., 2013). They do register how much air is sampled. So, thePOPs concentrations in the filtrate can precisely be related to the volume of air sampled. However, active samplers are much more expensive, need electrical power and more complicated to use. Another drawback is that the result is a reflection of the moment of sampling, normally only one day. The concentration might be different during the next week. This could be overcome by sampling in various weeks and taking the mean or median result. Of course, that adds to the number of samples to be analyzed. Corrections for wind directions could also be applied. As regards the accuracy of the data, active sampling no doubt has the preference. However, their use is not very cost- effective and requires training of staff in handling the machines and difficult to be deployed in background sites.

As passive air sampling is the recommended method in the GMP guidance and has been approved by Parties of the SC, changing this method is unlikely. Moreover, given the complexity and the associated costs, active sampling is not likely to be introduced as an alternative. Efforts should therefore be made to improve the passive sampling method. Several groups are working on better calibrations and other improvements of this method (Lazarov et al., 2013, Herkert et al., 2018, Melymuk et al., 2021). Prior to start sampling new POPs, it should be decided what the optimal length of the sampling period should be. Furthermore, temperatures and wind speed and direction should be monitored if possible. Duplicate or triplicate samplers should be used at one location. Internal reference compounds can be used to spike the PUF, to check if losses take place. Locations should not be changed from year to year. To compensate for the higher complexity and sampling and analysis costs, fewer locations could be used while also the selection of POPs could be limited (see 4.4).

4.2.2.Water

Water was added as a matrix to accommodate monitoring of PFAS. PFAS molecules contain a polar head in addition to a non-polar fluorinated carbon chain. That causes them to behave as a detergent. The challenge here is the variation in the chain length. The first two PFAS-POPs, PFOS and PFOA (perfluorooctanoic acid) had relatively long C-F chains (8 C-atoms). That makes them relatively nonpolar and allows bioaccumulation. Nowadays, shorter chain PFAS and oxygen containing PFAS (Brandsma et al., 2019) are being produced by industry which are less bioaccumulative and better water soluble. If those will also be listed in the SC as POPs, we will face a family of compounds with a large variety in polarity. Meanwhile, there are thousands of different PFAS compounds, of which hundreds are commercially used. Monitoring water will then present concentrations that will be dependent of the polarity of the compound. Taking a water sample is comparable to active air monitoring: it is a snapshot rather than an integrated value that is representative for a longer period. Taking water samples more frequently and using the mean/median value will solve this issue, but obviously requires more analyses. Instead of riverine samples, more remote locations and still waters such as lakes could be considered, to avoid strong fluctuations in the PFAS concentrations. Recently, reports have appeared that suggest that PFAS concentrate in sea spray. Although this is worrying, sea spray could maybe be considered as a useful tool for global trend monitoring. The AQUA-GAPs program uses passive water sampling to determine PFAS concentrations. That will integrate PFAS concentrations over time, nullifying possible peak concentrations. Passive water sampling may be useful for the purpose of determining spatial and temporal trends of POPs. A drawback is that they do not exactly reflectPOPs concentrations in fish and shellfish. Despite a lot of research (Booij et al., 2016), there is still an unexplained discrepancy between values found in passive water samples and in biota. However, that should not hinder the application of these samplers for trend studies.

4.2.3. Other matrices

As mentioned above, many matrices for global monitoring have been discussed in depth at the start of the GMP. Sediments would have been an option because those are globally available. Sediments do contain relatively high levels of POPs, provided they contain a relatively high carbon content. In some areas this causes limitations, as river sediments can be very sandy. If available, the next challenge is a proper clean-up of the sediment sample. Sulfur is normally present, and many other interfering substances need to be removed to create proper chromatograms. Dispatch of sediments around the world is also not very easy. Due to the possible introduction of unwanted microorganisms, this requires numerous permits from authorities that vary per country. These are normally only given after stringent microbiology rules have been implemented in a laboratory, which is quite an investment for a chemical laboratory. The same is true for soil samples. It renders sediments and soil less suitable for POPs monitoring unless they can be analyzed in the same country as where they were sampled. Other scientists have tried mosses, tree bark, dust, lichens, wristbands, other personal samplers, and other options. Most of these have not been tested worldwide. All of them have advantages and disadvantages which we will not discuss in detail here.

4.3. Target compounds

The list of POPs is growing by the year. Started with 12 chemicals/chemical mixtures ('dirty dozen'), meanwhile there are 34 POPs listed (Table 1) and more are expected (Fiedler et al., 2019). As long as chemicals are not tested before they can enter the market, new POPs will be invented and produced. If there should be one priority of the Stockholm Convention, it should be to globally establish such tests of chemicals prior to allowing them entering the markets. Until then, countries have to work with the existing POPs list. It is hoped that the GMP would show that some current POPs would vanish completely. Until now, such a success has not been recorded.

Having said that, we do see a downward trend for several POPs. During the recent UNEP GMP projects, many laboratories struggled to detect a number of POPs due to detection problems. Therefore, although northern regions, which may show higher POPs concentrations, were not included, there seems to be room for reduction of the GMP work by either lowering the frequency of monitoring of some POPs, or measuring them only at some locations, or leaving them out entirely. POPs added recently to the list should normally be measured because there is a lack of knowledge or uncertainty about their behavior. Unfortunately, that implies development of new methods, sometimes with new instrumentation. It emphasizes again the need for using mass spectrometers and labeled internal standards. Table 2 shows a proposal for discussion.

In this proposal, endrin, aldrin, the two chlordanes, heptachlor and its two epoxides, toxaphene, mirex, chlordecone, HBB, two HCHs, and PCNs are left out, mainly because of the low concentrations found during the last UNEP/GEF GMP projects. Admittedly, some of these POPs, such as toxaphene can still be found in northern regions. Chlordecone is left out because until now none of the reference laboratories has developed a proper method for it. From literature it is known that it mainly occurs in the West-Indies (Multigner et al., 2016), while in the 1970s it created a food scare in the James River (VA, USA) (Luellen et al., 2006). The HCHs can be represented by lindane (γ -HCH), normally the highest of the three isomers. Heptachlor, α - and γ -chlordene, and aldrin are almost never detected because they are metabolised very quickly. The heptachloro epoxide concentrations, especially those of α -heptachlor epoxide, are normally very low, which is also true for endrin, HBB, and mirex. For the PFAS group, only the main components PFOA, PFOS and PFNA should be analysed. PFNA has not been added to the POPs list but will likely be added and is part of the 'EFSA 4', which was proposed by the European Food Safety Authority (EFSA) and is used in many international reports as a guideline or food safety standard. The precursors (FOSAs and FOSEs) have rarely been found until now. A

frequency of monitoring has also been proposed in Table 2. Based on previous work, more frequent monitoring than once per 5 years seems unlikely. We have indicated that the most important POPs should be monitored on each occasion, but that for some (dioxins and furans, dieldrin, chlordanes, and PCNs) the frequency could be limited to only once per two occasions because the concentrations of these POPs are also low and will most likely decrease further. Finally, the number of locations has been cut back (see 4.5) and three categories have been suggested, 5, 8 or 18 locations. All together this will drastically cut costs of the monitoring work without losing essential information. The SCCPs, which were recently added to the POPs list, should preferably be analysed together with the medium-chain chlorinated paraffins (MCCPs – proposed for listing under the SC), because concentrations of both groups are substantial on many locations, they can easily be analysed together, and the MCCPs are likely to be added to the POPs list.

Name	SC Annex	Compounds included
PCDDs and PCDFs	С	210 congeners
PCBs	A, C	209 congeners, 6 indicators: nos. 28, 52, 101, 138, 153, 180
НСВ	A, C	1
DDT	В	p,p'DDT, o,p'-DDT, p,p'-DDE, o,p'-DDE, p,p'-DDD, o,p'-DDD
Dieldrin	А	1
Endrin	А	1
Aldrin	А	1
Chlordanes	А	α , β -chlordane, α , β -chlordene, trans and cis-nonachlor, oxychlordane
Heptachlor	А	Heptachlor, α , β -heptachlorepoxide
Toxaphene	А	>1,000 congeners, three indicators, nos. 26, 50, 62
Mirex	А	1
Tetra and penta-BDEs	А	six indicator nos. 47, 99, 100, 153, 154, 209 PBDE congeners,
Chlordecone (kepone)	А	1
НВВ	А	PBB153
PeCB	A, C	1
HCHs	А	α, β, γ-ΗCΗ
Hexa and Hepta-BDEs	А	BDE183
Endosulfan	А	α, β -endosulfan, endosulfan sulfate
HCBD	A, C	1
PCNs	A, C	75 congeners
РСР	А	Pentachlorophenol and its salts and esters
HBCD	А	3 diastereomers: α , β , γ -HBCD
DecaBDE	А	1
Dicofol	А	1
PFAS	В	PFOA, PFHxS, PFOS (and precursors FOSA, NMeFOSA, NEtFOSA, NMeFOSE,
		NEtFOSE)
SCCPs	А	>1,000 congeners, sum to be analysed
Dechlorane Plus	А	1
UV-328	А	1
Methoxychlor	А	1

Table 1. Current list of POPs

PCDD: polychlorinated dibenzo-*p*-dioxins; PCDF: polychlorinated dibenzofuran; PCB: polychlorinated biphenyl; HCB: hexachlorobenzene, DDT: dichlorodiphenyltrichloroehane; BDE: brominated diphenylether, HBB: hexabromodiphenyl, PBB: polybrominated diphenyl; PeCB: pentachlorobenzene; HCH: hexachlorohexane; HCBD: hexachlorobutiadiene; PCN: polycvhloronaphthalene, HBCD: hexabromocyclododecane; PFAS: per- and polyfluorinated alkyl substances; PFOS: perfluorooctanesulfonic acid; PFOA: perfluorooctanoic acid; PFHxS: perfluorohexanesulfonic acid; FOSA: perfluorooctanesulfonamide; FOSE: perfluorooctane sulfonamidoethanol; Nme: Nmethyl, Net: N-ethyl; SCCPs: short-chain chlorinated paraffins; UV-328: (2-(2H-benzotriazol-2-yl)-4,6-di-tert-pentylphenol). Annex A: Elimination; Annex B: Restriction; Annex C: Unintentional production.

T 0		1· · ·						
Ianie /	Pronoced	lict of	P()Pc to	he monito	red in ai	r in the	o coming di	ansa
	TTOPOSCU	1130 01			i cu ili ui		. coming u	cuuc.

РОР	Frequency (n/10yr)	Number of locations
PCDDs and PCDFs	1	6
PCBs (6 indicator PCBs)	2	18
НСВ	2	8
DDT (6 metabolites)	2	18
Dieldrin	2	8

α , β -chlordane, trans and cis-nonachlor, oxychlordane	2	8
PBDEs 47, 99, 100, 153	2	18
PeCB	1	6
γ-HCH (lindane)	2	8
α , β -Endosulfan, endosulfan sulphate	2	18
HCBD	2	8
DecaBDE	2	18
α, β, γ-ΗΒCD	2	18
PCNs	1	6
PFOA, PFOS, PFHxS, PFNA**	2	18
SCCPs*	2	18
Dechlorane Plus	2	18
UV-328	2	8

*If possible, to be analysed together with medium-chain chlorinated paraffins (MCCPs). **PFNA: perfluorononanoic acid.

4.4. Locations

Comments on the sampling locations, and especially on possible improvements and reduction of the uncertainties due to sampling have been made in 4.2.1. Duplicate or triplicate samplers should be used at one location. Internal reference compounds should be used to check if losses take place. Locations should not be changed from year to year. With that in mind, the number of locations can substantially be reduced. About 18 sampling stations, orderly distributed over the world in remote areas, far from possiblePOPs sources would be more than enough to follow globalPOPs trends, provided they are well-placed in remote areas and not influenced by local sources. Figure 1 shows a possible option. Fine areas from north to south are proposed, each containing three sampling locations, with one additional in the most industrialized zone. Two additional locations are added to cover the Pacific. Changes are of course possible, but every addition will obviously increase the costs of the programme. The locations, numbered from 1 to 18 in Figure 1 could be, e.g., three in the northern areas (e.g., Canada (1), northern Norway (2) and east-Russia (3)), four in densely populated and industrialized areas at the northern hemisphere in e.g., the USA (4), Spain (5), China (6) and Japan (7), three north of the equator (e.g., Barbados (8), Egypt (9) and southern India (10)), three south of the equator (e.g., Brazil (11), Uganda (12) and southern Indonesia (13)), three in very



Figure 1. Proposal for global distribution of air sampling points.

southern areas (e.g., Uruguay (14), Zambia (15) and southern Australia (16)), and two in the Pacific (e.g., Palau (17) and Kiribati (18)). The three in the north could possibly be covered by AMAP, and The USA sampling point by GAPS. Spain and Australia may be covered by the reference laboratories involved. The 11 sampling points in the northern hemisphere justify the higherPOPs load there, compared to the southern hemisphere where seven sampling locations are planned. It is a strong reduction of the programme, in which in the last round 43 points in just as many countries were sampled. Referring to Table 2, PCDDs and PCDFs, PeCB and PCNs should only be measured once per ten years on e.g., the locations 1 (Canada), 5 (Spain), 6 (China), 12 (Uganda), 14 (Uruguay) and 18 (Kiribati). For the six POPs that according to Table 2 should be analysed once per five years in eight countries, e.g., southern Indonesia (13) and Brazil (11) could be added. All other Pops should be sampled and analysed once per five years in all 18 locations.

4.5. Modelling options

With programmes generating so much data the question whether modelling can replace part of the programme is justified. Nowadays, with an ever-increasing power of computers and software programmes, one would expect that modelling would be able to help to predict the temporal trends in pollution by POPs. It is certainly worthwhile to explore the possibilities for modelling. However, this should not be related to the prediction of trends of POPs concentrations on GMP air monitoring stations. In the first place the data generated by the GMP air monitoring have currently a too high uncertainty to enable a meaningful modelling programme. To create useful models, quite a lot of data are needed, and that should be data with a relatively small uncertainty. The latter is obviously not available. The need for monitoring data based on chemical analysis would still be relatively high, so the gain in cost-effectiveness would be small. Finally, the POPs concentrations in air are dependent of – often political – decisions to clean disposal sites or terminate production and applications of POPs. Such events are impossible to predict by models.

However, modelling could play a useful role when related to the input, or, in other words, to the production of POPs. In fact, we have already a sort of model, i.e., the polychlorinated biphenyl (PCB) case. We know relatively precise that the entire world production has been ca. 1.3. million tons (UNEP, 2019b). No more PCBs are being produced. We have seen what type and size of effects these 1.3 million tons have caused, such as a decrease in the seal population, PCB levels in human blood and milk, etc. That model can be transferred, of course with adaptations, to other compounds. Although POPs are different, the PCB model would probably work for other aromatic chlorinated and presumably also brominated compounds. Possibly, for halogenated aliphatic compounds such as toxaphene and chlorinated paraffins, the effects would be different. For most POPs there are good estimates of the production. For example, we know that in China alone, more than 1 million tons of chlorinated paraffins are produced each year (Zeng et al., 2013). This is much more than the total volume of PCBs ever produced. For PFAS, we do not know how much has been produced until now. Efforts to achieve that knowledge are warranted. Once having those data, investing in modelling would be very helpful. Models should, however, never go without analysis as a check. In the Netherlands, under pressure of cuts in budget in the 1990s, the Public Institute for Health end the Environment (RIVM) switched almost entirely to modelling (RIVM, 2023). However, later it appeared that the models used were often not sufficiently validated due to a lack of chemical information, which made political decisions based on these models rather cumbersome.

5. Recommendations

The considerations in the previous chapters lead to six clear-cut recommendations.

- UNEP should continue to make use of the AMAP, GAPS and MONET global air monitoring data, possibly together with data generated by POPsEA and AQUAGAPS. In case investments in developing countries and full control on the strategy and ownership ofPOPs monitoring is desired, a separate, and more simple air monitoring programme, comprising ca. 18 locations, and with improvements (internal standards, duplicates, optimized PUFs, etc.) compared to the recently used sampling strategy, should be established.
- 2. Substantial cost reductions can be obtained by using fewer sampling points, a lower sampling frequency and a reduction of the number of POPs to be analysed.
- 3. Capacity building towards a full role in air monitoring of POPs of a selected number of laboratories in developing countries should be carried out. This should only be done under the two following strict conditions:
 - a. A firm commitment of the developing countries involved, laid down in a contract for ten years and penalties for no show.
 - b. Installation of GC/MS and preferably also LC/MS in the selected laboratories.

A meeting should be organized with donors, MS companies, scientists, and UNEP representatives to create a permanent solution for the problem of absent or not functioning MS instruments in developing countries.

- 4. Staff of the selected laboratories should be trained in chemical POPs analyses in reference POPs laboratories for at least half a year. The entire training program should last 1.5 year and include sampling and analysis of air samples by comparison with the reference laboratories. The monitoring stations of the selected laboratories should be maintained. The trained laboratories should function later as training centre for their region.
- 5. The ILS should be continued in a much-simplified form, with a frequency of once per two years. To reduce the costs and the workload of the laboratories and organizers, only be air extracts and human milk should be sent around as test materials.
- 6. Modelling can only be useful when related to the production volumes of POPs. PCBs can be taken as an example to predict POPs concentrations in the environment. By focusing on production volumes, it may also be easier to come to restrictions and bans of the POPs. In the end, fulfilling the main objective of the SC, protecting human health and the environment from POPs, can only be achieved when the production of all, including new POPs comes to a full stop.

6. Literature

- Belpaire, C.G.J., Goemans, G., Geeraerts, C., Quataert, P., Parmentier, K., Hagel, P., de Boer, J. (2009). Decreasing eel stocks: survival of the fattest. *Ecol. Freshwater Fish.* 18, 197-214.
- Booij, K., Robinson, C., Burgess, R.M., Mayer, Ph., Roberts, C.A., Ahrens, Allan, I.J., L., Brant, J., Jones, L., Kraus, U.R., Larsen, M., Lepom, P., Petersen, J., Profrock, D., Roose, P., Schafer, S., Smedes, F., Tixier, C., Vorkamp, K., Whitehouse, P. (2016). Passive sampling in regulatory chemical monitoring of nonpolar organic compounds in the aquatic environment. *Environ. Sci. Technol.* 50, 3–17.
- Brandsma, S.H., Koekkoek, J.C., van Velzen, M.J.M., de Boer, J. (2019). The PFOA alternative substitute GenX detected in grass and leaves near a fluoropolymer manufactory plant in the Netherlands. *Chemosphere* <u>220</u>, 493-500.
- De Boer, J., Hagel, P. (1994). Spatial differences and temporal trends of chlorobiphenyls in yellow eel (*Anguilla anguilla*) from inland water of The Netherlands. *Sci. Total Environ*. 141, 155-174.

- De Boer, J., Dao, Q.T., van Leeuwen, S.P.J., Kotterman, M.J.J., Schobben, J.H.M. (2010). Thirty year monitoring of PCBs, organochlorine pesticides and brominated diphenylethers in eel from The Netherlands. *Environ. Pollut.* 158, 1228-1236.
- De Boer, J., van Dijk, R., Abalos, M., Abad, E. (2023). Persistent organic pollutants in air form Asia, Afria, Latin America, and the Pacific. Chemosphere 324, 138271.
- Fiedler, H., van der Veen, I., de Boer, J. (2022). Assessment of four interlaboratory tests within the UNEP-coordinatedPOPs projects. *Chemosphere* 288, 132441.
- Fiedler, H., Kallenborn, R., de Boer, J., Sydnes, L.K. (2019). A tool for the global regulation of persistent organic pollutants. *Chem. Intern.* 41, 4-11.
- GMP (2023). <u>https://www.pops-gmp.org/gmp-dwh.html</u> (Acces. 9 March 2023).
- Göckener, B., Eichhorn, M., Lammer, R., Kotthoff, M., Kowalczyk, J., Numata, J., Schafft, H., Lahrssen-Wiederholt, M., Buckling, M. (2020). Transfer of per- and polyfluoroalkyl substances (pfas) from feed into the eggs of laying hens. part 1: analytical results including a modified total oxidizable precursor assay. *J. Agric. Fd. Chem.* 687, 12527-12538.
- Herkert, N.J., Spak, S.N., Smith, A., Schuster, J.K., Harner, T., Martinez, A., Hornbuclke, K. (2018). Calibration and evaluation of PUF-PAS sampling rates across the Global Atmospheric Passive Sampling (GAPS) network. *Environ. Sci.: Processes Impacts* 20, 210-219.
- Hung, H., Kallenborn, R., Breivik, K., Su, Y., Brorstrom-Lunden, E., Olafasdottir, K., Thorlacius, J.M., Leppanen, S., Bossi, R., Skov, H., Mano, S., Patton, G.W., Stern, G., Sverkko, E., Felin, Ph. (2010). Atmospheric monitoring of organic pollutants in the Arctic under the Arctic Monitoring and Assessment Programme (AMAP): 1993–2006. *Sci. Total Environ*. 408, 2854-2873.
- Kallenborn, R., Brevik, K., Eckhardt, S, Lunder, C.R., Manø, S., Schlabach, M., Stohl, A. (2013). Long-term monitoring of persistent organic pollutants (POPs) at the Norwegian Troll station in Dronning Maud Land, Antarctica. Atmos. Chem. Phys. 13, 6983-6992.
- Lazarov, B., Swinnen, R., Spruyt, M., Goelen, E., Stranger, M., Desmet, G., Wauters, E. (2013). Optimisation steps of an innovative air sampling method for semi-volatile organic compounds. Atmos. Environ. 79, 780-786.
- Leslie, H., van Bavel, B., Abad, E., de Boer, J. (2013). Towards comparable POPs data worldwide and analytical capacity building in Africa, Central and Latin America, and the Pacific. TrAC Trends Anal. Chem. 46, 85-97.
- Lohmann, R., Muir, D., Zeng, E.Y., Bao, L.-J., Allan, I.J., Arinaitwe, K., Booij, K., Helm, P., Kaserzon, S., Mueller, J., Shibata, Y., Smedes, F., Tsapakis, M., Wong, C.S., You, J. (2017). Aquatic global passive sampling (AQUA-GAPS) revisited: first steps toward a network of networks for monitoring organic contaminants in the aquatic environment. Environ. Sci. Technol. 51, 1050-1067.
- Luellen, D.R., Vadas, G.G., Unger, M.A. (2006). Kepone in James River fish: 1976–2002. Sci. Total Environ. 358, 286–297.
- Malisch, R., Kype, K., Kotz, A., Wahl, K., Bitomsky, N., Park, S., Tritscher, A., Lee, S.Y., Magulova, M., Fiedler, H. (2010). WHO/UNEP-coordinated exposure study (2008-2009) on levels of persistent organic pollutants (pops) in human milk with regard to the global monitoring plan. Organohal. Cpds. 72, 1766-1769.
- Melymuk, L., Bohlin-Nizzetto, P., Harner, T., White, K.B., Wang, X., Tominaga, M.Y., He, J., Li, J. Ma, J., Ma, W.L., Aristizábal, B.H., Dreyer, A., Jiménez, B., Muñoz-Arnanz, J., Odabasi, M., Dumanoglu, Y., Yaman, B., Graf, C., Sweetman, A., Klánová, J. (2021). Global intercomparison of polyurethane foam passive air samplers evaluating sources of variability in SVOC measurements. Environ. Sci. Pol. 125, 1-9.
- MSFD (2023) https://www.marine.ie/site-area/areas-activity/marine-environment/marinestrategy-framework-directive (Acces. 27 February 2023).
- Multigner, L., Kadhel, Ph, Rouget, F., Blanchet, P., Cordier, S. (2016.) Chlordecone exposure and adverse effects in French West Indies populations. Environ. Sci. Pollut. Res. 23, 3–8.
- Norén, E. (2023). Population exposure to organic contaminants and human biomonitoring. PhD thesis, Faculty of Medicin, Lund University, Sweden.

- OSPARCOM (2023). https://www.ospar.org/about (Access. 27 February 2023).
- Ougier, E., Ganzleben, C., Lecoq, P., Bessems, J., David, M., Schoeters, G., Lange, R., Meslin, M., Uhl, M., Kolossa-Gehring, M., Rouselle, C., Lobo Vincente, J. (2021). Chemical prioritisation strategy in the European Human Biomonitoring Initiative (HBM4EU) – Development and results. Intern. J. Hyg. Environ. Health 236, 113778.
- POPsEA (2023). https://wedocs.unep.org/bitstream/handle/20.500.11822/31005/5-CStu1_EAJapan.pdf?sequence=1&isAllowed=y (Acces. 27 February 2023).
- RIVM (2023). https://www.rivm.nl/en/consumer-exposure-to-chemical-substances/exposure-models
- Schuster, J.K., Harner, T., Eng, A., Rauert, C., Su, K., Hornbuckle, K.C., Johnson, C.W. (2021). Tracking POPs in Global Air from the First 10 Years of the GAPS Network (2005 to 2014). Environ. Sci. Technol. 55, 9479-9488.
- United Nations Environment Programme (2019a). Stockholm Convention on Persistent Organic Pollutants (POPs). Text and annexes, revised in 2019. Article 1., Geneva, Switzerland.
- United Nations Environment Programme (2019b). Global Chemicals Outlook II From Legacies to Innovative Solutions: Implementing the 2030 Agenda for Sustainable Development. ISBN no: 978-92-807-3745-5, Geneva, Switzerland.
- United Nations Environment Programme (2023). Organization and Outcomes of Four Interlaboratory Assessments on Persistent Organic Pollutants. Geneva.
- Wania, F., Shunthirasingham, C. (2020). Passive air sampling for semi-volatile chemicals. Environ. Sci.: Processes Impacts. 22, 1925-2002.
- Wells, D.E., de Boer, J. (2006). Evaluation of the quality of measurement of organochlorine contaminants in the marine environment: the QUASIMEME experience. TrAC Trends Anal. Chem. 25, 350-363.
- White, K.B, Kalina, J., Scheringer, M., Pribylova, P., Kukucka, P., Kohoutek, J., Prokes, R, Klánová, J. (2021). Temporal trends of persistent organic pollutants across africa after a decade of MONET passive air sampling. Environ. Sci. Technol. 55, 9413-9424.
- WFD (2023). https://water.europa.eu/freshwater/europe-freshwater/water-framework-directive (Acces. 27 February 2023).
- Zeng, L., Chen, R., Zhao, Z., Wang, T., Gao, Y., Li, A., Wang, Y., Jiang, G., Sun, L. (2013). Spatial distributions and deposition chronology of short chain chlorinated paraffins in marine sediments across the Chinese Bohai and Yellow Seas. Environ. Sci. Technol. *47*, 11449-11456.