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Global monitoring of persistent organic pollutants (POPs) in biota, water and sediments: its role in screening for unregulated POPs, in compiling time trends of regulated POPs under the Stockholm Convention (SC) and their relevance for biodiversity in a changing climate

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This paper considers elements of the dynamic process of production dispersal and monitoring of persistent organic pollutants in the environment that has unfolded over the past 100 years. The interactions between science, industry, policy making and public health have taken many different forms in different parts of the world over time. The current state of affairs of Persistent Organic Pollutants (POPs) in the global environment is only partially understood and in flux because the components act in a distributed and asynchronous manner. We argue that the work under the Stockholm Convention (SC) since 2004 can be seen as synthesis of what has been done so far and a blueprint of what challenges lie ahead. The framework of UNEP, with the invaluable help of the Secretariat, has strung together over two decades a global network of scientists, indigenous groups, policy makers and other stakeholders interacting through meetings, documents and decisions, this effort has yielded an open, transparent and reliable method of work and a large repository of publicly available technical and scientific information. In this paper we consider in some detail the methods and the outcomes for screening substances of new potential concern, the methods and outcomes of monitoring trends in the context of effectiveness evaluation of the SC and the urgent need to converge in concept and quantification with the Convention on Biological Diversity (CBD) and the Framework Convention on Climate Change (FCCC).

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#### **Environmental significance**

This paper considers the dynamic landscape in which global environmental monitoring and regulation of persistent organic pollutants has unfolded over the recent past. The objective of the paper is to highlight the quality and value of the work achieved and how it could help addressing the challenges shaping the work ahead. The paper is based on two recent compilations published under the Stockholm Convention on POPs (SC). The focus is on identifying monitoring data in biota and abiotic media that have been helpful in identifying and tracking substances of global concern. The first document considered was adopted at a recent meeting of the POPs Review Committee, POPRC19 and is a critical analysis of how long-range environmental transport is conceptualized and has been assessed for all listed POPs under the SC since 2004. The other is the latest Global Monitoring Report under the Effectiveness Evaluation of the SC, which also indicates a number of new concepts, methods and challenges that need to be addressed. The paper does not introduce original research or empirical data, it attempts to sketch the efforts involved in advancing the possibility for a fair, wise and global strategy for chemical management, biodiversity and climate change, based on empirical observation and reaching consensus on shared understandings and priorities.

# 1 Introduction

There is a very long line of efforts to track and predict changes in the environment, to build shared knowledge about what has happened, and attempt to predict what might happen. Current efforts by academic institutions, governments, NGOs and Multilateral Environmental Agreements (MEAs) to monitor

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POPs in environmental samples belong to that long lineage of social constructs. These cooperative efforts strive to integrate a growing set of observations with forms of effective heuristics, models of reality that help interpret the observations of the past and allow accurate predictions. We will address briefly the scientific, conceptual and institutional background to large scale environmental monitoring and identify important challenges today concerning mixtures, long range environmental transport (LRET) and cooperation between MEAs. The historiography of monitoring the environment and the related

computational and quantification efforts to do so is an active field of research.<sup>1,2</sup> The description and understanding of the extent to which monitoring and quantification have occurred in all parts of the world for millennia interacting on a global scale is in itself a historical process. What is thought today about the history of science, technology and culture disputes and undermines forms of hegemony that dominated the field from the 19th century.<sup>3</sup>

Social changes in science, technology and culture over recent decades have changed the environment, the ways to monitor it and the social processes in which science and technology unfold.

It has been well established that by end of the 19th century a number of social and technological procedures changed the chemical landscapes first locally then regionally and globally through a dispersion cloud, a halo, that started around high energy density infrastructures burning coal and oil, and discarding waste in the atmosphere and water. That waste was in part processed into useful chemical products such as organohalogens. 1 By the 1970s all corners of the planet had been touched by novel artificial, toxic chemicals in air and water. For the first time in 4000 million years all organisms on Earth are exposed to larger or smaller amounts of organohalogens that have been, and are artificially produced in large volumes for their useful properties. Several of these chemicals are persistent, volatile under certain conditions, accumulate in cells and organisms, magnify along trophic pathways, and have negative effects on ecosystems and health interfering with cellular metabolism, endocrine development and function with negative effects on neural, immune and hormonal development. The chemical history of present times can be read in sediments, sample banks and long term monitoring efforts as an outcome of the history of chemistry over the past fifty years.

By the late 1960s a number of studies in Finland and beyond showed that Cs137, that could only come from nuclear tests, was accumulating in lichens, reindeers and native Sami populations in the Arctic. This made the consideration of long range atmospheric transport as a major pathway for contaminants a central issue. The improvements in chromatography and mass spectroscopy, as well as the invention by J. Lovelock in 1957 of the electron capture detector, allowed for pioneering studies on PCBs and DDT in birds and fish in the Arctic. 4,5 The new insights on the global presence of traces of organohalogens and the concurrent impact of several major accidents (PCBs in Yusho in Japan, 1968, dioxines in Seveso Italy 1976, and others) left no doubt that acute and chronic exposure to organohalogens was deleterious, toxic, and dangerous for human health and the environment. A number of local and regional regulations were introduced concerning a few chemicals that had shown to be present in significant concentrations in air, water and organisms.

Meteorology had changed by the 1920s with the use of telegraph and radio, allowing the perception of large scale patterns in short time intervals (synoptic patterns) and a new understanding of the weather. The development of chemical weapons in the early 1900s went together with the development of atmospheric transport models. The institutions and people

who developed the early quantitative air dispersion models for chemical weapons used monitoring data and Lagrangian models of dispersion in the troposphere. Chemical weapons were banned in 1918 on moral principles and also because they had shown to be ineffective. The scientists and institutions that had been involed on atmospheric research in that context moved, in the 1940s to monitor and model nuclear explosions. Nuclear test provided invaluable unique tracers to demonstrate the fast long range transport of molecules in the atmosphere at hemispheric scales. In the 1960s hundreds of atmospheric nuclear tests were carried out and the outcomes can be measured in any dated sediment, and in fact the signals from the early 1960s have been frequently used to date sediment cores. A large community emerged able to compute and calibrate long range atmospheric transport models.

The Norwegian Meteorological Service under the leadership of Anton Eliassen in cooperation with many others developed the co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe (unofficially 'European Monitoring and Evaluation Programme' = EMEP), a scientifically based and policy driven programme under the 1979 Convention on Long-range Transboundary Air Pollution (CLRTAP) for international co-operation to solve transboundary air pollution problems (https://www.emep.int).8 EMEP deployed in a few years a network of over 100 stations across Europe that work under the same protocols and share QA/QC. The data (ebas/nilu.no) resulting from this network, which is still very much operational, were paired from the beginning with increasingly detailed and elaborate models of long range atmospheric transport of pollutants and monitoring and modelling impacts on ecosystems. Many of the concepts and models developed in radiation protection in the 1950s were adapted to deal with acidification, and other long range transboundary transport of air pollution (LRTAP) problems such as  $NO_x$ , ozone, heavy metals and POPs in the 1980s.

By the 1990s it was well established that major LRTAP issues could only be dealt within a binding international framework where monitoring and modelling were done in a coherent, consistent and transparent manner.

Over the last 100 years the chemistry of the environment, what is out there and what is known about it has significantly changed. The international scientific understanding and policy response to those challenges has also changed and has resulted in a number of long term national, regional and global cooperative efforts. It is relevant to note that those long term efforts unfold over decades in a dynamic environment in which the scientific tools and understanding change and the policy environment changes, while the situation on the ground is also changing.

In recent times these dynamic interactions have yielded a sequence of international policy frameworks that have shown to be effective and will need much more work in the future. In 1979 the UNECE LRTAP convention was signed by 48 countries in the northern hemisphere as a binding treaty to address long range transboundary transport of air pollutants, including a regional monitoring and assessment framework EMEP. In 1972 the US and Canada signed the Great Lakes Water Quality

Agreement (GLWQA), the Baltic Marine Environment Protection Commission - also known as the Helsinki Commission (HEL-COM) agreement on the Baltic was signed by all countries in the basin in 1974, in 1991 the Arctic Council established Arctic Monitoring and Assessment Programme (AMAP) with the participation of all Arctic countries and a representation from indigenous communities. The Convention for the Protection of the Marine Environment of the North Atlantic (OSPAR) was established in 1992 integrating two agreements started in 1972 with the Oslo Convention against dumping and was broadened to cover land-based sources of marine pollution and the offshore industry by the Paris Convention of 1974. These two conventions were unified, updated and extended by the 1992 OSPAR Convention. The new annex on biodiversity and ecosystems was adopted in 1998 to cover non-polluting human activities that can adversely affect the sea.

Severe pollutions caused by rapid industrialization motivated Japan to establish the Environment Agency in 1971, which was reorganized as Ministry of the Environment in 2001 to expand its scope. Among the early activities of the agency was the establishment of Act on the Regulation of Manufacture and Evaluation of Chemical Substances, which put priority of regulation on persistent and bioaccumulative toxicants (PBT or POPs), and the start of environmental monitoring, which focused on POPs in biota and later in sediments, in 1973. Japan also established National Institute for Environmental Studies (NIES) in 1974 and National Institute for Minamata Disease in 1978. Both institutes have been conducting monitoring research actively over decades including the Environmental Specimen Bank at NIES archiving various research samples as well as specimens of governmental POPs monitoring at  $-60\,^{\circ}\mathrm{C}$ .

The Framework Convention on Climate Change (FCCC) and the Convention on Biological Diversity (CBD) were adopted at the 1992 United Nations Conference on Environment and Development, Rio de Janeiro, Brazil. This global conference was held on the occasion of the 20th anniversary of the first Human Environment Conference in Stockholm, Sweden, in 1972.

In 1997 the Great Lakes Health Effects Program, in Health Canada released: State of Knowledge Report on Environmental Contaminants and Human Health in the Great Lakes Basin.<sup>9</sup> This document identifies subpopulations at higher risk and describes a pioneering monitoring and assessment strategy for a number of contaminants: organochlorines, metals, radionuclides, microbes and airborne contaminants and considers the weight of evidence for the ecotoxicological impact on ecosystems and health from these multiple contaminants.

In 1997 AMAP presented the Assessment Report: Arctic Pollution Issues. <sup>10</sup> This large volume was innovative and had a very significant impact, it included a chapter with a detailed description Peoples of the Arctic: Characteristics of Human Populations Relevant to Pollution Issues, that laid out the contours of the very important work AMAP and many other institutions in the Arctic have done communicating with native communities. <sup>11</sup> The report also presented a pioneering integrated consideration of different contamination types and routes including detailed chapters on POPs, heavy metals (Pb,

Cd, Hg), radioactivity, acidification, petroleum hydrocarbons, climate change and human health.

Both of these major compilations by Health Canada and AMAP integrated into a coherent frame the outcome of research in monitoring and assessment of the different contaminants that was initiated in the late 1960s in many cases in relation with accidents and spills. A number of ideas emerged from these compilations that shaped the development of international agreements, first the great importance of long range transboundary atmospheric and marine transport, which implied that any effective strategy to deal with these contaminants had to be global, multilateral and binding, as had been already understood for radiation and acidification and made the evidence for long range environmental transport (LRET) a central criterion to list a substance as persistent organic pollutant (POP) under the UNEP Stockholm Convention on POPs. The other clear evidence was that some vulnerable groups were highly exposed to contaminants in any society, vulnerable groups sometimes at great distances from the sources, and almost always far from the benefits resulting from the production and use of contaminants. Fairness and equity issues emerge from ecotoxicology and public health.

In 1998 UNECE LRTAP adopted the Århus protocol on Persistent Organic Pollutants, subsequently UNEP initiated negotiations for a global treaty that became the Stockholm Convention on POPs, which was signed in 2001 and entered into force in 2004 and today (August 2023) has been ratified by 186 parties.

# 2 The Stockholm convention on POPs

The SC today provides an interesting detailed precedent for science policy interactions.<sup>12</sup> Its operation and outcomes over the past decades highlight the relevance of a few central components, such as the steady long term contributions of dedicated people in laboratories and public institutions, the central role of natives and vulnerable groups to focus attention and action, the work of the secretariat making the meetings possible and the generation of consensual, rigorous and public documents. These elements are the base to address current challenges, that include refining the monitoring and interpretation of LRET and enhancing the cooperation and coherence with other MEAs that address the risk of chemicals to the environment and health such as CBD and FCCC.

In this paper we consider a few examples of the role environmental monitoring has played in shaping the SC and how monitoring data, and what kind of data can help assess and improve the effectiveness of actions to reduce the risk of POPs to the environment and health.

In the text of the SC monitoring is considered under several articles, we focus here on articles 8 and 16. Article 8 outlines the review process for new chemicals. The Persistent Organic Pollutants Review Committee (POPRC) is a subsidiary body of the Stockholm Convention established to review chemicals proposed for listing in Annex A (elimination), B (restriction),

and C (unintentional production). The POPs Review Committee consists of 31 government-designated experts drawn from the regions as follows: African States: 8, Asian and Pacific States: 8, Central and Eastern European States: 3, Latin American and Caribbean States: 5, Western European and other States: 7.

The text of the Convention specifies the information required for the review in Annex D, E, and F. Detailed descriptions of the process for reviewing chemicals proposed for listing (https://chm.pops.int/tabid/2806/Default.aspx), as well as the risk profiles and risk management documents (https://chm.pops.int/tabid/243/Default.aspx) adopted by the Committee, can be found on the Stockholm Convention website.†

The two processes, the review of new chemicals by POPRC and long term monitoring for Effectiveness Evaluation under the Global Monitoring Plan (GMP) have different objectives, time frames and methods of work. These differences are, as we will see, complementary and synergistic in several ways.

#### 2.1 The screening under Article 8

The outcomes of the review process under article 8 to list new substances in Annex A (elimination), B (restriction), C (unintentional production) by POPRC since 2004 are described in detail in the document adopted at POPRC19 2023: "Consideration of longrange environmental transport when evaluating chemicals proposed for listing under the Stockholm Convention".<sup>13</sup>

The overall outline of the process led by the POPRC is as follows, after receiving a proposal by a Party or group of Parties to include a chemical in Annex A, B and/or C to the Convention as a persistent organic pollutant (POP), "the Committee examines the proposal and applies the screening criteria specified in Annex D in a flexible and transparent way, taking all information provided into account in an integrative and balanced manner". When the POPRC is satisfied that the screening criteria are fulfilled the committee is tasked to develop a Risk Profile (RP) in accordance with Annex E. When the RP has been adopted by the committee the following task is to develop a Risk Management Profile (RMP) in accordance with the guidance in Annex F. Between 2009 and 2023, 22 chemicals, or groups of chemicals, were listed and another three are being reviewed at the Annex E or Annex F stage.‡ The RMP adopted by the Committee is then submitted to the COP that might introduce changes before adopting its decision about listing. The document (ref. 13) describes in detail how these steps were completed for each of the 22 new chemicals or group of chemicals listed after 2009.

The screening criteria specified in Annex D for a proposed substance include (a) to establish its chemical identity, (b)

assess its persistence, including observed half lives in water, soil and sediment, (c) its bioaccumulation, (d) long range environmental transport, and (e) adverse effects. The convention states that a party submitting a proposal to list a substance shall "provide the information on the chemical, and its transformation products where relevant to the screening criteria".

We will consider with some detail the monitoring information compiled to apply the screening criteria (d) in relation with long range environmental transport.

The text of the convention states that the screening should establish:

- (d) potential for long-range environmental transport:
- (i) measured levels of the chemical in locations distant from the sources of its release that are of potential concern;
- (ii) monitoring data showing that long-range environmental transport of the chemical, with the potential for transfer to a receiving environment, may have occurred *via* air, water or migratory species; or
- (iii) environmental fate properties and/or model results that demonstrate that the chemical has a potential for long-range environmental transport through air, water or migratory species, with the potential for transfer to a receiving environment in locations distant from the sources of its release. For a chemical that migrates significantly through the air, its half-life in air should be greater than two days; the detailed analysis of the available information that has been used in the screening indicates the kind of questions that arise and what forms and methods of monitoring have been helpful.<sup>13</sup>

According to ref. 13 "Since the entry into force of the Convention, 28 new chemicals or groups of chemicals proposed for listing have met one or more of the screening criteria for potential for LRET. The appendix summarizes the key evidence on which POPRC concluded that LRET screening criteria are met or not met for these chemicals, as outlined in the POPRC decisions".

The consideration of d(i) "measured levels of the chemical in locations distant from the sources of its release that are of potential concern" brings up two important points, the assessment of the distance from sources (measured levels of the chemical in locations distant from the sources of its release) and the contours of "potential concern".

The assessment of the distance from sources is today a very active field of work, in terms of the models to estimate it (see below) and the changing nature of the sources, including itinerant consumer and industrial products that can be local sources in remote locations. The understanding of "potential concern" has moved from a single substance approach and limited ecotoxicology, to a dynamic field considering mixtures, transformation products and impact of POPs on biodiversity in a changing climate.

The consideration in ref. 13 (para 20 and below) of the central issues for a clear definition of measured levels, includes analytical techniques, reliability, detection limits, sampling methods and their validation. Consideration is also needed of the quantity, as well as quality of monitoring data available for a particular substance. Under the GMP a guidance document is regularly updated to address some of these questions.<sup>14</sup> More

 $<sup>\</sup>dagger$  Organohalogens (also known as halocarbons) are a class of organic compounds that contain at least one halogen (fluorine [F], chlorine [Cl], bromine [Br], or iodine [I]) bonded to carbon. Some are produced naturally like dioxins in volcanos and wood burning, or methyl bromide produced by marine algae. Some substances that are not organohalogens have POP-like characteristics (e.g., PAHs, rubber additives such as 6PPD, UV filters).

<sup>‡</sup> A complete and updated list of all chemicals listed can be found in https://www.pops.int/TheConvention/ThePOPs/AllPOPs/tabid/2509/Default.aspx

recently, standard operating procedure (SOP) and protocols developed under the UNEP/GEF GMP2 project have been outlined and are available: https://www.unep.org/explore-topics/chemicals-waste/what-we-do/persistent-organic-pollutants/capacity-building-gmp2.

Agreement on methods and standards for environmental sampling of currently listed POPs and substances of global concern is a continuing and dynamic task. POPRC for each risk profile considers monitoring data reported in all media, air, water, snow, ice, soil sediment, biological samples and Environmental Sample Banks (ESBs), concerning that substance in locations far from sources.

The evaluation and assessment of "distant from sources" entails a number of problems that have become more pressing with the new substances and modes of transport and release. The POPRC is constrained by the limited geographical coverage of available monitoring data of newly proposed substances or groups of substances, at the time of listing. The GMP can and has improved significantly the global coverage of available monitoring data on a chemical once it is listed in the SC.

It is interesting to note here and in other points below that over time the understanding of the nature and the position of the sources relative to the monitoring sites has changed. In addition, the understanding of exposure pathways and endpoints has changed in profound ways since the early 2000 when this work was established. A clear, rigorous, and general understanding of these issues today and in the future is needed to advance towards the objectives of the SC and the wider cooperation with CBD and FCCC.

The consideration of d(ii) "Monitoring data showing that long-range environmental transport of the chemical, with the potential for transfer to a receiving environment, may have occurred *via* air, water or migratory species" implies a shared understanding of transport models in air, water, migratory species as well as the potential to be received there.

The document on LRET<sup>13</sup> (para 35) summarizes in Table 1 the sampling locations considered in previous POPRC work as far from sources and in Table 2 the sampling locations of monitoring data that previously supported the evaluation of LRET and transfer to a receiving environment, as outlined in POPRC decisions, and states that "monitoring data was available for all chemicals that have been reviewed by POPRC up to 2022". Some exceptions include chlordecone and dicofol. Monitoring data for these chemicals in remote locations were limited: dicofol was detected in the Arctic in only one study and it was not obvious whether that result was used to meet criterion (i) or (ii). Apart from the Arctic, monitoring data from remote regions are, however, in general limited and time-trend data are not always available or are often not directly comparable due to differences in sampling location, sample matrix, analytical methods, and/or time-period for when the monitoring was performed (see Box 1 in UNEP 2023 for further considerations). One possible approach to address some of the limitations identified is to consider data obtained from Environmental Specimen Banks, which may provide an appropriate series of samples in remote areas to investigate temporal trends of chemicals of concern, by retrospective analysis. Care should be

given with these samples due to the differences in collection and handling procedures specific for the chemical(s) and species of interest.

In many cases, the POPRC considered the data for criteria 1(d)(i) and 1(d)(ii) together. This was the case with decisions on hexabromobiphenyl (HBB), perfluorooctane sulfonic acid (PFOS), short-chain chlorinated paraffins (SCCPs), pentachlorobenzene (PeCB), hexabromocyclododecane (HBCD), polychlorinated naphthalenes (PCNs), hexachlorobutadiene (HCBD), dicofol, Dechlorane Plus, UV-328, chlorpyrifos, and  $C_{14-17}$  chlorinated paraffins at >45% Cl.

The document<sup>13</sup> (para 17 and below) considers in detail the challenges involved in monitoring and assessment of travel by air in gas, particles, ice and snow. The main degradation pathway in air is photo-oxidation and the rate is often not well characterized and will change depending on how exposed the molecule is, the presence and meaning of precursors and transformation products is a very important issue that has taken more weight recently with new analytical and modelling tools (Table 3).<sup>15</sup>

For some POPs (e.g., HCH, PFAS) water can be the main transport pathway, to remote locations, sediments and deep ocean sinks, and it has been shown that the role of dissolved or suspended organic matter and the microbiome in them is central in the dispersion of POPs.<sup>16-18</sup>

The text in ref. 13 (para 70) indicates that sediments have also been suggested to undergo long-range transport with turbidity currents, <sup>19</sup> and in para 71 "Hydrophobic POPs such as PCBs and PBDEs have been detected in organisms living in Hadal trenches, which are the deepest parts of the ocean". <sup>20,21</sup> Even the deepest ocean fauna (>10 000 metres) was found to have levels of POPs that are considerably higher than those documented for nearby regions of heavy industrialization. <sup>22</sup> It has been shown that PCB concentrations were 5–10 times higher in the intermediate and deep-water masses of the Arctic Ocean than in surface waters. <sup>23</sup>

Migratory species, including birds, fish and marine mammals, undergo seasonal long-distance migrations and can release POPs in remote areas such as breeding grounds with a significant negative impact on biota and humans. The total mass of a given POP transported by animals to a remote location is always much smaller than the mass transported by abiotic media, air, water, and can be difficult to attribute to that pathway in any given location<sup>13</sup> (para 84 and references therein).

The monitoring data compiled are then to be analysed in terms of d(iii) "Environmental fate properties and/or model results that demonstrate that the chemical has a potential for long-range environmental transport through air, water or migratory species, with the potential for transfer to a receiving environment in locations distant from the sources of its release. For a chemical that migrates significantly through the air, its half-life in air should be greater than two days".

The focus of the text of the Convention here is on assessing potential for LRET and transfer to receiving environments. 
<sup>13</sup> (para 102): Models provide supporting scientific evidence when applying the screening criteria in Annex D to the Convention, and when evaluating environmental fate, monitoring, and

Table 1 Commonalities and differences between POPRC and GMP

	Objective	Method of work	Outcomes	Time frames
Art 8, POPRC	Screening for newly proposed POPs of global concern	POPRC reviews available scientific literature concerning all media	Risk profile, risk management profile	The adoption of a listing decision by the COP, concludes the work of POPRC on that substance
Art 16 EE and GMP	Monitoring changes over time of global concentrations of listed POPs in core media (air, serum, milk and water for PFOS/PFOA)	Regional organization groups (no. 5) of nominated 6 experts compile every 6 years a Regional Report including approved data from air human samples and water in the region and submit to the COP. The GCG develops a Global Report	The Global Monitoring Report baselines and time trends constitute one of the pillars of the Effectiveness Evaluation	GMP includes newly listed POPs at successive iterations (2009, 2015, 2023) and continues to trace all POPs listed earlier, as far as practicable

exposure information requirements in Annex E to the Convention. Models can also ascertain the LRET potential of sources that have not been measured in remote locations and contribute to develop monitoring to target those substances and locations to confirm that finding.

It has been shown over decades that a very effective strategy to characterize and address large scale, transboundary environmental issues, such as acidification, eutrophication, tropospheric O<sub>3</sub>, particulate matter (PM), and black carbon, is to work in integrated modelling frameworks, including models of emission rates, transport, deposition and effects, operating together.<sup>24</sup> The application of the integrated approach to modelling POPs has been proposed and tested.<sup>13</sup> Para 103 notes that when used as part of an integrated approach, models can be viewed as a framework for assembling a repository of knowledge and conceptual understanding about POPs in the environment<sup>25–27</sup> and in this sense also help to identify knowledge gaps to be refined and improved, including today's understanding of LRET and the links with biodiversity and climate change.

For screening purposes a number of models have been developed to predict from the chemical structure and properties of a substance their potential for Long Range Transport Potential (LRTP). The metrics that are used in modelling can focus on the potential to travel long distance in a medium (air, water) or consider the tendency for a chemical to accumulate in the receiving environment. Para 105) cites as examples of the former the Characteristic Travel Distance and the Spatial Range, Spatial examples for the latter are the Transfer Efficiency and the Arctic Contamination Potential (2003, 2007).

A recent proposal<sup>34</sup> integrates a transport-oriented metric for the extent to which the chemical reaches a remote region, with a target-oriented metric for the extent to which the chemical is transferred to surface media in the remote region, with one that quantifies the potential for accumulation in the surface media in a remote region. The resulting three metrics are coherent and account for both transport in air and water<sup>13</sup> (para 106).

The document<sup>13</sup> (para118) states that "Several international working groups have been formed in recent years to explore and evaluate fate and transport modelling capabilities, to identify knowledge and data gaps, and to make recommendations for

Table 2 Sampling locations considered distant from sources or remote in the POPRC decisions of chemicals on Annex D screening phase (from ref. 13 Table 1)<sup>a</sup>

Locations	Chemicals
Arctic, including Arctic Ocean	Alpha-HCH, beta-HCH, dicofol, HBB, HBCD, lindane, PCNs, PeCB, decaBDE, dechlorane plus, HCBD, methoxychlor, PCP, PFOA, PFOS, PFHxS, SCCPs. UV-328, chlorpyrifos, $C_{14-17}$ chlorinated paraffins at >45% Cl*, long-chain $C_9$ - $C_{21}$ PFCAs <sup>b</sup>
Turkey Lakes, Ontario; Kejimkujik, Nova Scotia;	PFOA ("three remote areas" in Environment Canada and Health Canada,
and Chapais, Quebec (Canada)	2012)
Lake Superior	UV-328
Tibetan Plateau	Dechlorane Plus
Southern Atlantic	UV-328
Antarctica/Antarctic Ocean	Alpha-HCH, PCNs, Dechlorane Plus, endosulfan, methoxychlor, PFOS, PFHxS, chlorpyrifos, long-chain C <sub>9</sub> -C <sub>21</sub> PFCAs

<sup>&</sup>lt;sup>a</sup> That the committee does not always specify all data taken into account in the consideration. <sup>b</sup> The proposal by Canada (UNEP/POPS/POPRC.17/7) covers PFCAs with carbon chain lengths from 9 to 21 inclusive, their salts and related compounds. For the sake of readability these are referred to as "long-chain  $C_9$ – $C_{21}$  PFCAs" covering also salts and related compounds.

Table 3 Origin of monitoring data used to support POPRC decisions on Annex D para 1(d)(ii) that long-range environmental transport of the chemical may have occurred (from ref. 13 Table 2)<sup>a</sup>

Locations	Chemicals
Arctic	HBB, alpha-HCH, beta-HCH, PentaBDE, lindane, PCNs, decaBDE, Dechlorane Plus, endosulfan, HCBD, methoxychlor, octaBDE, PCA $^b$ , PFOS, PFOA, PFHxS, UV-328, chlorpyrifos, $C_{14-17}$ chlorinated paraffins at >45% Cl*, long-chain $C_0$ – $C_{21}$ PFCAs
Arctic/North Atlantic	HBCD, PeCB, SCCPs
Arctic/North Pacific Ocean	Dicofol, PFOS, methoxychlor
Lake Superior	UV-328
Tibetan Plateau	Dechlorane Plus
Southern Atlantic	UV-328
Antarctica/Antarctic Ocean	Alpha-HCH, PCNs, Dechlorane Plus, methoxychlor, PFOS, chlorpyrifos, long-chain PFCAs

<sup>&</sup>lt;sup>a</sup> That the Committee does not always specify which data are used to conclude on the criterion. <sup>b</sup> Pentachloroanisole (PCA) is a metabolite of pentachlorophenol (PCP).

research priorities. Notable efforts include the 2010 Assessment Report of the Task Force on Hemispheric Transport of Air Pollutants, 24,35 which was formed under the Convention on Long-range Transboundary Air Pollution in 2010, the Saltsjöbaden V workshop,36 the workshop on Next Generation Air Quality Monitoring,37 the final report of the ArcRisk EU FP7 Collaborative Project,38 and ref. 39".

The final item (e) on the screening criteria in Annex D is to ascertain "Evidence of adverse effects to human health or to the environment that justifies consideration of the chemical within the scope of this Convention". This aspect is beyond the scope of this paper, but it must be noted that it is a very active field of research and new insights and empirical data in analytical chemistry, as well as molecular and cell biology in the context of very large and dynamic data repositories (see for instance ref. 40 and CBD Nagoya and Konming protocols§) will ground any coherent understanding of the impact of chemicals on ecosystems and health, and lead to a better understanding of the relationship between exposure to chemicals in the environment, public health, biodiversity and climate change. There are very good long time series of monitoring data on POPs and contemporary time series of climate data, only a small fraction has been investigated together indicating a potentially very rich field of research.41

When the POPRC is satisfied that the screening criteria in Annex D are fulfilled for a chemical or group of substances the committee is tasked to develop a risk profile (RP) in accordance with Annex E; when the RP has been adopted by the committee

§ The Convention on Biological Diversity (1992). CBD, in article 7 of the Identification Monitoring convention: and (https://www.cbd.int/convention/articles/default.shtml?a=cbd-07) Monitoring Framework for the Kunming-Montreal Global Biodiversity Framework (https://www.cbd.int/gbf/targets), including Target 7: Reduce Pollution to Levels That Are Not Harmful to Biodiversity, the Nagoya protocol under CBD (https://www.cbd.int/abs/default.shtml). The CBD and FCCC are closely intertwined in their objectives and method of work with the Basel Rotterdam Stockholm and Minamata processes. The relationships of chemical pollution with ecosystem function and structure as seen in biodiversity indicators and with geophysical variables in climate change and LRET are of central interest.

the next task is to develop a Risk Management Profile (RMP) in accordance with the guidance in Annex F. The appendix in ref. 13 describes the details of how these steps were completed for the 22 new chemicals or group of chemicals listed after 2009.

The laborious monitoring work in remote locations, often relying on cooperation with local native minorities, has preceded and grounded the awareness that mobilized the SC and the POPRC which with the competent help of the Secretariat has delivered rigorous and effective guidance to the COP over the past 20 years.

#### 2.2 Effectiveness Evaluation and Global Monitoring Plan

Effectiveness Evaluation in article 16 establishes a process to inform the COP about the outcomes of the measures undertaken "to protect human health and the environment from persistent organic pollutants". According to article 16 of the Stockholm Convention, the effectiveness of the Convention shall be evaluated on the basis of available scientific, environmental, technical and economic information, including:

- Reports and other monitoring information on the presence of POPs and their regional and global environmental transport.
  - National reports submitted pursuant to Article 15.
- Non-compliance information provided pursuant to Article 17.

The framework for effectiveness evaluation¶ was adopted at COP6 (2013) and the EEC committee established at COP7 (2015) by decision SC-7/24. The EEC completed a first cycle (2010-2016) and a second cycle (2017-2023). || The EE can be understood as a global effort to advance towards a comprehensive mass balance of POPs.

Once a risk profile and a risk management profile for a substance have been adopted by POPRC and the COP, the work of POPRC moves on to new candidate substances and the GMP is tasked with compiling the best available information on

<sup>¶</sup> https://www.pops.int/Implementation/EffectivenessEvaluation/Framework/ tabid/139/Default.aspx

 $<sup>\</sup>parallel https://www.pops.int/Implementation/EffectivenessEvaluation/$ Outcomes/2023Outcomes/tabid/9559/Default.aspx

Table 4 Monitoring programmes contributing data to the GMP. Source: Table 2 in the third regional monitoring reports under the global monitoring plan<sup>42</sup>

Region	Air	Human tissues	Water	Other media
Africa	Global atmospheric passive sampling (GAPS) network	UNEP/WHO human milk survey	MONET-Africa pilot project	Limited monitoring dealing with the contamination of water, soil, sediments and foodstuffs by POP pesticides
	MONET-Africa UNEP/GEF GMP I and II projects		UNEP/GEF pilot project and GMP II project	UNEP/GEF GMP projects
Asia-Pacific	POPs monitoring project in East Asian Countries (POPsEA)	China monitoring programme on human milk	United Nations University (UNU-IAS)/Shimadzu project (2018)	Japan national monitoring programmes on water, ground water, bottom sediments, soil, biota, foodstuffs
	China national POPs monitoring programme Japan national monitoring programme MONET-Fiji UNEP/GEF GMP I and II projects GAPS network	Japan POPs monitoring programme on human milk Japan monitoring programme on human blood UNEP/WHO human milk survey	National water monitoring programmes: China, Japan UNEP/GEF GMP II project	UNEP/GEF GMP II project (national samples)
EE	APOPSBAL  Arctic monitoring and assessment programme	UNEP/WHO human milk urvey	Joint Danube Survey (2009, 2013 and 2019) Aqua MONET-Europe	National programmes on <i>e.g.</i> , soil, sediments and biota are available in the region but rather variable,
	(AMAP) GAPS network European monitoring and evaluation programme (EMEP) MONET-Europe MONET-EE		NORMAN Association	episodic
GRULAC	GAPS network Latin passive air monitoring network (LAPAN) UNEP/GEF GMP I and II projects	UNEP/WHO human milk survey	UNEP/GEF GMP II project	UNEP/GEF GMP II project (national samples)
WEOG	AMAP	AMAP	AMAP	AMAP
	Australia's Casey station	Australian human biomonitoring	International Council for the Exploration of the Sea (ICES) database	Australian Pilot Monitoring Programme
	Australian National Passive Air Sampling and Archiving Program	Spain Biomonitorización de Contaminantes en la Población Española (BIOAMBIENT.ES)	Peer reviewed literature	Great Lakes GLB
	ЕМЕР	USA National Health and Nutrition Examination Survey (NHANES)	National programmes in Canada, Finland, and Australia	HELCOM
	GAPS network	Canadian Health Measures Survey (CHMS)	Helsinki Commission/The Baltic Marine Environment protection Commission (HELCOM)	OSPAR
	Great Lakes Basin Monitoring and Surveillance Program (GLB)	German Environmental Survey	NORMAN EMPODAT database	MEDPOL
	Integrated Atmospheric Deposition Network (IADN)	Swedish national monitoring program	Convention for the protection of the marine environment of the North-East Atlantic (OSPAR)	AM
	MONET-Europe	UNEP/WHO human milk survey	Mediterranean Pollution Monitoring and Research Programme (MEDPOL)	
		Peer reviewed literature	-	

Table 4 (Contd.)

Region	Air	Human tissues	Water	Other media
	Monitoring Network in the		Australian Pilot Moni	toring
	Alpine Region for Persistent		Programme	
	and other Organic Pollutants		C	
	(MONARPOP)			
	National Air Pollution		ICES database	
	Surveillance (NAPS)			
	Northern Contaminants			
	Programme (NCP)			
	Norwegian Troll Station			
	Spanish monitoring			
	program on POPs			
	Swedish national			
	monitoring programme for			
	air			
	Toxic Organic Micro			
	Pollutants (TOMPs) program			
	UK-Norway SPMD Transect			

changes over time of listed POPs every 6 years (GMP1:2009, GMP2:2015, GMP3:2021). For each of the 31 substances and groups of substances listed under the SC there are a publicly available, extensive and detailed risk profile and a risk management profile, these documents provide a very good summary of what monitoring evidence was available and helpful at the time of listing. The GMP reports inform about the current state of knowledge for listed POPs in core media.

Article 16 states the commitment by the COP to the "establishment of arrangements to provide itself with comparable monitoring data on the presence of the chemicals listed in Annexes A, B and C as well as their regional and global environmental transport". By 2006 the 5 regional organization groups (ROGs) (Africa, Asia Pacific, Latin America and the Caribbean (GRULAC), Central Europe and Western Europe and other groups (WEOG)) each composed of 6 experts nominated by parties in the region were established and the Global Coordination Group including 3 members of each group delivered the regional reports and the global report was compiled from them.

The COP decided in 2004 that the GMP would focus on core media (air, human biomonitoring serum and milk, and since 2009 PFOS and PFOA on water). This decision does not exclude other media, but in terms of compiling comparable long term data, air, human samples (serum, milk) and water for PFOS and PFOA are prioritized. Air samples, especially in remote locations, provide the fastest indication of the potential impact of measures undertaken by the SC. For some chemicals (HCH, PFOS, PFOA) water can be the dominant vector for LRET, although the response time is considerably longer and can be impacted by other factors than current or recent releases. Human biomonitoring by monitoring internal exposure to POPs is the primary objective of the convention.

Monitoring other media, such as water, snow, ice, soil, sediment and biota is central to understanding transport pathways and exposure to POPs, and, as noted above, is also

needed in terms of screening substances that are of new global concern, and in terms of a coherent understanding of the ecotoxicology of chemical landscapes and potential impacts on ecosystem structure, function and human health in a changing climate.

The GMP has relied for its compilation of time trends in air and human samples delivered by well established long term monitoring programs, Table 4 below lists the main strategic partners that have contributed to GMP3.<sup>42</sup> The compilation of PFOS and PFOA mesurements in water since 2009 (GMP2) has relied on an extensive and careful review of available reports and peer reviewed scientific literature.<sup>48</sup>

The GMP3 report<sup>42</sup> on other media, including biota, water, ice, snow, soil and sediment has relied on work by long term monitoring programs in biota and has also addressed the importance of ecosystem modelling to interpret changes in concentrations in biota.<sup>26,43–46</sup>

We cite below the main conclusions on other, non-core media of the GMP3 in ref. 13 (paragraph 91).

A significant volume of high-quality data on POPs in non-core-media such as snow, ice, sediment, soil and biota (invertebrates, fish, birds, mammals) monitored over several decades is available in some areas such as the Great Lakes, the Arctic, the Baltic, and Japan and could be studied along with climate change variables over the same period.

The overall picture seemed to be consistent and indicated that levels of the initial POPs remained relatively low, dominated by secondary sources and unchanged since the second GMP report in 2015. Although less documented, newly listed POPs (*e.g.*, tetrabromodiphenyl ether and pentabromodiphenyl ether (PBDEs), PFOS, SCCPs, HCBD, HBCD, PCNs) do not show decreasing trends, they show at best that increases are slowing. The levels were relatively low compared to the initial POPs (PCB, HCHs, DDT) a decade ago, but the growing presence of other POPs was of concern.

Table 5 Summary of temporal trends of POP concentrations in other media. Table designed by K. Borgå, M. Røyset Aarønes, and Y. Shibata in the GMP3 report<sup>42 $\alpha$ </sup> (paragraph 97)

	Northern Hemichhere				Southern Hemisphere		
	AMAP	AMAP	OSPAR	HELCOM	Great Lakes	Japan (fishes)	
	(1975–2000)	(2001–2014)	(1995–2014)	(1978–2018)	(1970-2017)		(NA)
Aldrin	О	О	О	О	О	o	О
α-НСН							
β-НСН							
Chlordane	1					o	
Chlordecone	О	О	О	О	О		О
DDT		1				О	
Dieldrin						О	
Endosulfan	О	О	О	О	О		О
Endrin	О	О	О	О	О	О	О
ү-НСН						o	
Heptachlor						О	
HBB	Δ	Δ	Δ	Δ	Δ	Δ	Δ
HBCD					3	Δ	
Hexa-, hepta-BDE			2	2	3	O	
HCB							
Mirex			О	0	О	-	О
PeCBz							
PFOS					3	Δ	
PCB						o	
PCDD							
PCDF							
Tetra-, penta-BDE					4	0	
Toxaphene		5				-	
HCBD							
PCP	Δ	Δ	Δ	Δ	Δ	Δ	Δ
PCN						0	
DecaBDE						Δ	
SCCP	Δ	Δ	Δ	Δ	Δ	Δ	Δ
Dicofol	Δ	Δ	Δ	Δ	Δ		Δ
PFOA						Δ	
PFHxS	Δ	Δ	Δ	Δ	Δ	Δ	Δ

<sup>&</sup>lt;sup>a</sup> (1) One local source (whale processing site) causes an increasing trend in some species; (2) BDE-153 and BDE-154 only. (3) Increasing in some lakes, decreasing in other lakes; (4) overall decreasing, increasing in whole fish in Lake Erie and in sediments in Lake Superior; (5) parlar 26 decreases annually by 5.9%, parlar 50 increases annually by 0.8%. Across the regions, alpha-, beta- and gamma-HCH, DDT, PCB, tetra to heptaBDE showed decreasing trends, and/or decreasing/no change. No substances showed increasing trends across all regions; however, in the Great Lakes, HCB, HCBD, PCNs and decaBDE in general showed increasing trends, as well as DDT in Antarctica, and HCB in the Baltic region. Dieldrin and toxaphene were reported by both AMAP and GLWQA, showing decreasing levels or nonlinear trends. PFOS was reported across several regions, with contrasting trends: increasing in the Arctic and the Great Lakes and decreasing in the Baltic region and the North Atlantic.

Environmental specimen banks including biological samples and analytical extracts from sampling media have shown to be helpful and cost effective to establish temporal trends and screen potential of new chemicals of concern.

Regular and comprehensive efforts to compile and report comparable regional and global data on POP monitoring should be prioritized as such data can provide best empirical base to improve knowledge about POP pathways and the changes in space and time of the risk posed by POPs to humans and the environment.

Multimedia ecosystem modelling is central to interpreting biological data and can help design effective monitoring strategies.

In the GMP3 the Africa and Eastern Europe regional reports included some relevant data from the literature; the Asia Pacific and WEOG regional reports could rely on a small number of long term monitoring efforts that have compiled time series for a number of POPs in biota, water, soil and sediment. Table 5 below presents a summary of these results.

# Closing remarks

We have briefly considered the background and current applications of environmental monitoring work for screening chemicals of global concern and to assess the effectiveness of measures undertaken under the UNEP Stockholm Convention. Many limitations and innumerable shortcomings can be identified from the records and compilations produced by the SC and help to address current challenges. The operation and outcomes of the SC over the past few decades highlight the relevance of few central components, such as the steady long term contributions of dedicated people in laboratories and public institutions, the long term stability, consistency and international cooperation in monitoring has proven to be indispensable and requires funding, public support and credit for its work.

The central role of natives and vulnerable groups to focus attention and action has shown to be a main driver of the SC11,47 and has contributed immensely at all stages of monitoring and assessment of the risk posed by POPs. The urgent need for a coherent integration of work on chemicals, biodiversity and health will only make this contribution more relevant in the future.

Much credit should be given to the gigantic work of the UNEP secretariat preparing and making the meetings possible and generating consensual, rigorous and public documents from them. The corpus of information on POPs and related substances, edited and maintained in transparent and accessible repositories by the secretariat as well as the networks of cooperation and collegiality that produce these documents and policy outcomes is incomprehensible without that competent and kind work.

New tools, new ideas and a growing understanding of environmental chemistry and biology in recent decades present resources, challenges and problems that can be addressed on a global, fair, transparent and rigorous process of cooperation and inclusion. The workings of the SC since 2004 are a small part of it entwined with a large network of MEAs including the Convention of Basel (on chemical waste), Rotterdam (on trade of chemicals), Stockholm (on POPs) and Minamata (Hg), the Convention on Biological Diversity, the Framework Convention on Climate Change (FCCC), as well as regional and national efforts aiming to monitor and decrease the risk of toxic chemicals to the environment and health enhancing coherence and cooperation between those efforts are urgent and possible.

# Disclaimer

The opinions expressed in this paper are the author's and do not represent any of the institutions mentioned.

#### Author contributions

RG: conceptualization, writing the first draft, review and editing, and as lead in the work on other media in the WEOG report and Global report in GMP in 2009, 2015 and 2021.

## Conflicts of interest

There are no conflicts to declare.

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