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# How Enhancing Atmospheric Monitoring and Modeling can be Effective for the Stockholm Convention on POPs

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**Abstract:** The presence of toxic substances such as persistent organic pollutants (POPs) in the environment, and in organisms including humans, is a serious public health and environmental problem, even at low levels and poses a challenging scientific problem. The Stockholm Convention on POPs (SC) entered into force in 2004 and is a large international effort under the United Nations Environment Programme (UNEP) to facilitate cooperation in monitoring, modeling and the design of effective and fair ways to deal with POPs globally. This paper is a contribution to the ongoing effectiveness evaluation (EE) work aimed at the assessment and enhancement of the effectiveness of the actions undertaken under the SC. First we consider some aspects related to the monitoring of POPs in the environment and then briefly review modeling frameworks that have been used to simulate long range transport (LRT) of POPs. In the final sections we describe the institutional arrangements providing the conditions for this work to unfold now and some suggestions for it in the future. A more effective use of existing monitoring data could be made if scientists who deposited them in publicly available and supervised sites were rewarded in academic and professional terms. We also suggest the development of multi-media, nested, Lagrangian models to improve the understanding of changes over time in the environment and individual organisms.

**Keywords:** POPs monitoring; modeling; Stockholm Convention effectiveness; Global Monitoring Plan

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## 1. Introduction

The Stockholm Convention on POPs (SC) entered into force in 2004 and currently has 178 parties [1]. This international agreement under UNEP was established as a consequence of the perceived environmental and social risk posed by a number of toxic substances produced and intentionally or unintentionally released to the environment in large volumes. These substances are toxic to humans and other organisms, are persistent, and can travel long distances in the atmosphere and in some cases also water. They accumulate in organisms and concentrate along food chains. The ambition of the SC is to promote international coordinated action to decrease the presence of these substances in the environment and humans. A central aspect in the SC is the EE process under which the Global Monitoring Plan on POPs (GMP) has been working since 2008. The GMP aims to compile the best available data on POPs and stimulate consistent and high quality monitoring of levels of POPs in biotic and abiotic environmental matrices and their changes over time.

Due to their hydrophobic nature POPs tend to accumulate from the abiotic environment into organisms and concentrate along food webs [2]. One important consequence is that very low environmental concentrations can build up to harmful concentrations inside the body through long term exposure. Due to their low rates of degradation in the environment and in organisms they can have negative impacts a very long time after their release and the exposure [3]. Their volatility is a function of temperature among other things meaning that they can be deposited from the atmosphere and re-emitted to it under changing climate or geographic conditions [4]. Their similarity in chemical structure with molecules that play central roles in very small quantities in the endocrine systems of organisms in early stages of life [5,6] results in the need to gauge very small quantities in the environment and organisms.

The use of POPs as pesticides, industrial chemicals and the unintentional releases in combustion processes are spread all over the world in diffuse sources and products; consequently control measures cannot be limited to a few industrial sectors or activities. These differences with other environmental contaminants such as metals, ground level ozone, stratospheric ozone depleting substances and green house gases (GHG) mean that the measuring, modeling and control of POPs pose specific and new challenges to the international community of scientists, policy makers, regulators and the public at large.

Early restrictions of several POPs started around four decades ago, with the ban and control at a national or regional level of some substances (including Mirex, dieldrin, DDT, and Polychlorinated biphenyls (PCBs)). Since then an increasing number of global, regional and national initiatives aiming at reducing and regulating the use and releases of POPs have been put in place. For instance, international monitoring of POPs was initiated in the North American Great Lakes in 1990 and by the Arctic Monitoring and Assessment Programme (AMAP) in 1993 [7]. A few years later in 1998 the first international agreement on POPs was signed in the United Nations Economic Commission for Europe (UNECE) under the Convention on Long-range Transboundary Air Pollution (CLRTAP) [8]. Subsequently the UNEP governing council decided to initiate the negotiation of a global agreement that was signed in Stockholm in 2001 and entered in to force in 2004. The SC establishes a process to identify substances that qualify as POPs, the possible alternatives for their uses and modes of control. The SC agrees on reporting obligations by parties, and encourages technology exchange, capacity building and financial arrangements between parties. In addition, the SC establishes a framework to evaluate the effectiveness of the measures undertaken.

Four sections are presented below. In the first section we introduce a few general ideas on monitoring and modeling, and their implications in terms of the practical questions concerning POPs that monitoring and modeling might help to address. In the second section we present a brief review of existing frameworks for modeling the long range transport and fate of POPs. In the third section we describe the institutional framework and how theoretical ideas, ongoing monitoring and modeling efforts can converge to increase knowledge on POPs and enhance the effectiveness of the SC. The fourth section presents some concluding remarks and a strategy for the further development of the EE process under the SC.

## 2. Monitoring and Modeling POPs in the Environment

A number of international programs have measured POPs in air since the 1990s (see Table 1) and a growing number of research projects report data on POPs in published scientific literature [4] (pp. 195–205), [9]. In addition, several regional and global models, briefly described below, have been applied and compared to one another. A number of international efforts such as the Global Atmospheric Watch (GAW) and Global Earth Observation (GEO) under the World Meteorological Organization (WMO), the Task force on Hemispheric Transport of Air Pollution (HTAP) under WMO and the UNECE-CLRTAP and the Global Monitoring Plan (GMP) under the UNEP SC on POPs have been working towards using the best available knowledge to develop effective observation and environmental management practices.

### *2.1. A few Notes on Measuring and Modeling Ecosystems*

Measuring and monitoring the environment is a dynamic, distributed and performative process where objects, ideas and gestures interact in a coordinated social effort by individuals and institutions to build knowledge (see for example detailed studies in China in [10], Mexico [11], The High Atlas [12] or La Garrotxa [13]). Measuring is deceptively difficult. Techniques have to be tested, established, and agreed upon; units have to be standardized and convertible; and the technical enterprise has to be conceptualized, organized, and transmitted across time and space. This knowledge is based on the interaction of regulated observations and abstract and material models that synthesize these observations. One important point is the idea that measurements are relational, that is, part of a relation and not absolute appraisals, as clearly expressed by Ernst Mach in 1871 [14] (p. 61): "Since we only recognize what we call time and space by certain phenomena, spatial and temporal determinations are only determinations by means of other phenomena. If, for example we express the position of earthly bodies as functions of time, that is to say, as a function of the earth's angle of rotation, we have simply determined the dependence of the position of the earthly bodies on one another. The same holds of space. We know positions in space by the affection of our retina, of our optical or other measuring apparatus and our x, y, z in the equations of physics are, indeed, nothing else than convenient names for these affections: Spatial determinations are, therefore, again derivations of phenomena by means of other phenomena". This observation had a central role in the mathematical physics of the last century [14].

Monitoring environmental quantities and modeling the physical world to describe and understand the observed features can be imagined as sequential operation of concepts and tools to construct registered point events. In the words of Jagjit Singh, [15] (p. 173): "Physics is mainly concerned with events, such as the arrival of a light ray at a particular point, the explosion of an atom, the emergence of a nova, *etc*. To be able to talk about events in the same way as we talk about points in geometry, we need a method for assigning registration marks to these events. This is easy, for every event must take place somewhere and sometime. So if we took the coordinates of the point of its occurrence and watched the instant of time at which it occurred we would have a complete set of specification marks to identify the event. Every point or "point-event" to use geometric terminology, has therefore a set of four numbers $x_1$, $x_2$, $x_3$, $x_4$ to identify it."

Monitoring is the compilation of "point-events" where each point event has its list of registration marks, assigned by registration rules. Registration rules are different forms of measurement, or specification of point events that allow them to be located in their specificity and amalgamated into larger data clusters and models.

To analyze the composition of a given sample a number of laboratory instruments, techniques and chemical standards will be used. The results will be meaningful only if it can be shown that the analytical methodology has followed certain rules and procedures. In this sense measuring implies the application of a sequence of concepts and local models concerning the workings of instruments and procedures to gauge one aspect of the environment by taking and treating local samples according to agreed quality assurance/quality control (QA/QC) protocols. The written outcome of this is then related to data processing and large scale modeling with the intention of building operative knowledge. If we can say this piece of cloth is 1.3 m long or we have sampled 1 $m^3$ of air this is the result of a long story of cooperation and invention linking individual performances and large scale cooperative work [16].

When a set of registered point events or measurements is studied, there are multiple strategies to explore the information in the data. These strategies can be based on inference, that is based on the observation of patterns in the data by statistically filtering out features of heuristic or predictive value. Alternatively they are devised to search in the data for observable behavior that agrees with a model parametrized to the local values. In practice it is always some combination of these approaches that operate (see for example [17,18]).

Point enumeration rules include algorithmic methods, applying sequences of rules to the data to extract features and also axiomatic principles searching for data that fit predicted or expected patterns. Different point enumeration rules, that is different frameworks and sets of procedures for attributing registration marks, will result in models and disciplines working with atoms, molecules, organism, ecosystems. In the fields where those points are localized, registered, there will be trajectories and transformation rules the point trajectories in the field are identified (in space time or phase space) by changes in the registration numbers of points in successive frames.

The systems of differential equations that are used in models of flow and turbulence in gas liquid or solids are simulating, computing the transformations of point events in space time or phase space trajectories. Singh [15] (p. 180) describes it:

> *Whether we study the motion of pendulum bobs or cannon balls, of planets or galaxies, of fluids in pipes or river beds, or winds in laboratory tunnels or over aircraft wings in the*

> *sky, stony solid particles like sand and gravel suspended in moving water in river and harbor models, or underwater missiles like depth charges, we have in the last analysis, to solve a set of one or more differential equations. In many cases the situation is so complex that it may not be possible even to frame the appropriate differential equation or set of differential equations. But our ability to frame it by no means implies our ability to solve it. In fact given a set of differential equations, the odds are heavy against its being amenable to any known treatment. That is why any new way of treating them is so valuable. Group Theory is valuable as it is the master key that solves a large class of equations that can be solved in no other way.*
>
> *Group-theoretical approaches owes it great power to the fact that equations of fluid motion remain invariant not only under the group of transformations of units but also in many cases under groups of transformations such as the group of rotations and translations. This however, is not all. The value of the group-theoretic approach in fluid mechanics does not only depend on its usefulness in solving the differential equations of fluid motion it is also the unifying principle in innumerable questions of fluid mechanics-as indeed it has proven to be in other branches of physics. For instance, it is the very core of modeling analysis whereby we use river, harbor, aerodynamic and other models to study actual fluid behavior experimentally to bridge the gap between hydrodynamical theory and experience.*

In atmospheric physics or oceanography many of the important features are scale invariant over a range of orders of magnitude and so tea cup eddies and oceanic currents share many dynamic features and can be described with the same basic model. One of the challenging complications of biology and ecosystems theory is that many important features are scale dependent, the conditions for their existence occur only at certain scale ranges, and certainly there are no bus sized bacteria or microscopic string orchestras.

The production and reproduction of local transient singularities such as macro molecules, cells, multi-cellular assemblages, organisms and ecosystems can be described as the present configuration of a continuous cascade of events. The sequences of events are confined by scale invariant limiting conditions and scale dependent forms of agency attached to and resulting of transient semi autonomous trajectory bundles. These bundles maintain and reproduce similar conditions at different scales and locations in space and time.

The occurrence of transient bundles at certain wavelengths in the overall turbulent flow is obvious in the sense that molecules, cells, organisms, populations and ecosystems can be observed, measured, classified by different criteria of similarity, described in registered point events and trajectories. The individual organism, enclosed in a skin and going, alone, through a life history plays an outsized role in the theory of ecology in models of foraging, niche, population and evolution. Individual organisms are obvious “point-events” but are not alone or isolated. Organisms and their assemblages exist as transient bundles navigating in a multiplicity of flows of matter and energy unfolding from cell metabolism to global bio geochemistry. There is an urgent need to integrate scale invariant theory of fluid dynamics and the concurrent operation of processes that are scale dependent and occur only at certain scales.

Scale dependent forms of agency or trajectory bundles prevalent in biology such as cells, organisms, populations and ecosystems, pose difficult problems to model on two counts: First they require scale specific probing, they are not invariant to a change in scale (if you want to understand bacteria you need to look at bacteria, you cannot deduce bacteria from your experience with tomatoes), and second, given the multiplicity of speeds at which perturbations propagate in different media, the outcome is local and stochastic and never exactly the same, and consequently the heuristic power, how much you can learn from the past, is limited. More limited, say, than if you study a set of balls on a flat table, a prism, a pipe, a mechanical device or an electric circuit.

In the framework of fluid dynamics where systems of differential equations describe the trajectories of registered point events the challenge is to develop models that are able to inscribe trajectory bundles and scale dependent forms of agency in the wider field of scale invariant fluid dynamics and turbulence.

The challenge, in theory and practice, to integrate trajectories in multiple media (gas, liquid, solid) interacting at multiple scales in operational models is relevant in scientific and in wider policy terms to model POPs pathways in the environment.

POPs are a serious problem and also good tracers [19], a theoretical problem that is also a public health issue. There is an urgent need for coherent and consistent databases and models ranging from molecular pathways (such as intrinsic degradation rates) to global atmospheric and oceanic transport. As POPs are tracers monitoring their trajectories in space and time indicates the routes and activity levels of relevant pathways in organisms and ecosystems. POPs include many substances with different chemical properties. They are, or have been, produced and dispersed in mixtures with many other substances and thus their study is synergistic with other biological and ecosystem research including classic air quality issues, such as criteria pollutants and heavy metals. Effective long term and large scale environmental protection strategies require a commensurate effort to compile and study monitoring and modeling data in integrated and cost effective strategies. Modeling the environmental transport (through air, water, organisms or commerce) of different substances is essential to design monitoring strategies that must identify sites to monitor the background and sites and to estimate activity of sources. Such work is, as we have seen, a distributed process based on agreements in theory and in practice on analytical, computational and reporting procedures.

### 2.2. Query of Available Data

What are the practical questions concerning the current status of POPs and the effectiveness of the measures undertaken that monitoring and modeling might help to address?

There are different kinds of data available for POPs and related compounds, including (a) regular and sporadic measurements in samples from the environment and organisms, (b) toxicology data from experiments and the field (for a very few POPs); (c) Chemical and biochemical information about many more substances; (d) Emission inventories (for a handful of substances); (e) transport and fate models; (f) effects models and (g) global and regional arrangements to handle the data and work on them. Some of the important challenges or questions today can be formulated as: (1) Baselines: what are the levels today or in the recent past and what changes can be observed (2) Mixtures: how to integrate information about multiple substances (3) Modeling of changes over time and effects of low doses.

### 2.2.1. Baselines

In 2009 the first Global Monitoring Report was presented to the fourth meeting of the Conference of the Parties to the Stockholm Convention (COP4) [20] reviewing the best available information on the 12 POPs listed at that time, it presented global information for a limited number of POPs (a list of the complete name of the substances and acronyms is given in Table 1) such as (PCBs, DDTs, HCHs) and other POPs (PCDD/Fs) only available with very limited spatial coverage (see Table 1). In 2010 an updated review was published in the HTAP 2010 Assessment Report [4]. In 2015 the GMP will present the next global report that should include the best available information on baselines for the currently listed POPs, including PBDEs, and PFOS. In recent years, partly as a result from UNEP and GMP initiatives, based on the deployment of passive air samplers, such as GAPS and MONET the global coverage for a number of POPs in air has significantly grown as well as the field and laboratory capacity in some regions [21,22]. There are still outstanding gaps and difficulties ahead, but significant progress has been made. One challenge here for the future is how to make best use of a good combination of data resulting from long term stable monitoring in remote regions, data from long term stable monitoring in urban industrial regions, and data resulting from intermittent, short term projects in both types of regions. The information about remote sites is valuable to protect the remote regions, for LRT studies and to as assess global changes over time. The information about urban or industrial sites is valuable to identify sources and exposure routes to large populations.

In this context the development of structures that give professionally effective credit to valuable monitoring contributions deposited in supervised public repositories could be very helpful. A further challenge is to maintain and develop agreements on what substances and what congeners are traced, can be traced, have been traced, which brings us the following point, the consideration of contaminant mixtures.

### 2.2.2. Mixtures

Most current monitoring, modeling and regulation are sequentially focused on individual target substances. However, the nature of the problem as well as the available analytical and computational tools, all indicate that more integrated models are feasible and meaningful. At one level for instance in active and passive air samples, the concentration values in a (active/passive) sample are difficult to compare in meaningful ways. Global scale air monitoring of POPs has become feasible through passive samplers. In a passive sampler an integrated sample is taken over a long period of time and it is difficult to know exactly what volume of air was sampled. In high volume active samplers the accuracy and precision of the air concentration estimate for the sampled period are much better, but there is a large uncertainty on the concentration between the limited sampling periods. On the other hand the composition of the sampled mixture of substances and congeners and its relative weights in a passive or active sample are quite legitimately comparable in quantitative ways. At another level, the work on emission inventories, on alternatives and Best Available Techniques/Best Environmental Practice a well as in estimating cost and benefits of control measures would certainly benefit from having better tools to monitor and model mixtures of pollutants including POPs from their release to transport in the environment to exposure and effects.

**Table 1.** Adapted from Table A.2.1. (pp. 195–197) in Appendix A of Chapter 2 of UNECE (2010) [4], lists major programs monitoring POPs in air, the methods and substances monitored that contributed to the SC GMP 2009 report.

| **Monitoring Program** | **Abbreviation** | **Region of Interest** | **Number of Sites** | **Period** | **Sampling Method** | **Monitored Compounds *** |
|---|---|---|---|---|---|---|
| Arctic monitoring and assessment programme | AMAP | Arctic | 12 (includes 8NCP sites) | 1993–present | Active/non-directional | PCBs, HCB, HCHs, chlordanes, DDTs Additional compounds at 8 NCP-operated sites (see below). |
| Northern Contaminants Program (Canada) (part of AMAP) | NCP | Arctic | 8 (part with AMAP) | 1992–present | Active/non-directional | PCBs, DDTs, PAHs, PentaCB, mirex, chlordanes, HEPT, HEPX, PeCB, HCB, HCHs, endrin, aldrin DIEL, ENDO 2002–present: PBDEs November 2000–Feburary 2001: PCDD/Fs 2006–present, Alert station: PFCs |
| European Monitoring and Evaluation Programme | CLRTAP-EMEP | Europe including Russia | 18 in 2007 (includes 3 AMAP sites) | 1991–Present | active/nondirectional (12 sites with air and precipitation measurements 6 sites with air only) | As of 2007: PCBs, DDTs, chlordanes, HCB, PAHs, HCHs, HEPT, DIEL |
| Global Atmospheric Passive Sampling network | GAPS | Global | 52 (current operation) 95 (since inception) | 2004–present | Passive (PUF disk/XAD/sorbernt impregnated PUF (SE | PCBs, chlordanes, DDTs, HEPT, HEPX, HCHs, DIEL, PBDEs, ENDO 2005: PCNs 2009 at 20 sites: PFCs |
| Integrated Atmospheric Deposition Network (US&Canada) | IADN | Great Lakes | 8 (3 in Canada, 5 in USA) | 1990–present | active/non directional | PCBs, chlordanes, ENDO, HCHs, DDTs, HEPT, HEPX, aldrin, endrin, DIEL, HCB, MIREX, PAHs; 2002–present: PBDEs 1995–2005 at Lake Ontario, Canada only: Toxaphene |
| Integrated Atmospheric Deposition Network (US&Canada) | IADN | Great Lakes | 8 (3 in Canada, 5 in USA) | 1990–present | active/non directional | PCBs, chlordanes, ENDO, HCHs, DDTs, HEPT, HEPX, aldrin, endrin, DIEL, HCB, MIREX, PAHs; 2002–present: PBDEs 1995–2005 at Lake Ontario, Canada only: Toxaphene |
| Integrated Atmospheric Deposition Network (US&Canada) | IADN | Great Lakes | 8 (3 in Canada, 5 in USA) | 1990–present | active/non directional | PCBs, chlordanes, ENDO, HCHs, DDTs, HEPT, HEPX, aldrin, endrin, DIEL, HCB, MIREX, PAHs; 2002–present: PBDEs 1995–2005 at Lake Ontario, Canada only: Toxaphene |
| NationalAir Pollution Surveillance (Canada) | NAPS | Canadian Urban | 18 stations | 1969–present | active/nondirectional | PCP, HCB, PAHs, PCBs, PCDD/Fs, PBDEs |
| Monitoring Network in the Alpine Region for Persistent and other Organic Pollutants | MONARPOP | European Alpine regions | 3 active air monitoring stations (out of 40 sites) | 2004–present | active/directional (3 stations); passive (SPMD) | PCBs, DDTs, HCB HEPT, DIEL, aldrin, endrin, mirex, PCDD/Fs, HCHs, PAHs, PBDEs |

**Table 1.** *Cont.*

| **Monitoring Program** | **Abbreviation** | **Region of Interest** | **Number of Sites** | **Period** | **Sampling Method** | **Monitored Compounds *** |
|---|---|---|---|---|---|---|
| National Dioxin Air Monitoring Network (US EPA) | NDAMN | USA | 34 | 1998–2004 | active/non directional | PCDD/Fs, co-planar PCBs |
| New Jersey Atmospheric deposition Network | NJADN | USA | 9 | 1997–2001 | active/non directional | PCBs, PAHs, DDTs, HCHs, ENDO, aldrin, DIEL |
| New Jersey Atmospheric deposition Network | NJADN | USA | 9 | 1997–2001 | active/non directional | PCBs, PAHs, DDTs, HCHs, ENDO, aldrin, DIEL |
| Xarxa de Vigilància i Previsió de la Contaminació Atmosfèrica | XVPCA | Catalonia (Spain) | 28 | 1994–present | Active/non-directional | PCDD/Fs, 2003-present:PAHs, co-planar PCBs |
| National POPs monitoring network (MONET) | MONET | Europe, Asia, Africa, pacific Islands | Total number of sites deployed to date 245 | 2006–present | passive (PUFdisk); active/nondirectional (at Kosetice) | PAHs, PCBs, HCHs, DTs, HCB, PeCB, at selected sites/dates dioxins |
| Chinese POPs Soil and Air Monitoring Program (SAMP),Phase I | SAMP-I | China rural, urban | 97 (4 background, 24 urban, and 69 rural) | 2005–2007 | passive (PUFdisk) | PCBs, chlordanes, DDTs, HEPT, HEPX, HCHs, DIEL, ENDO, PAHs, PBDEs |
| Chinese POPs Soil and Air Monitoring Program (SAMP), Phase II | SAMP-II | China urban, rural, background | 12 urban and 4 background | 2008–present | Active/nondirectional | PCBs, chlordanes, DDTs, HEPT, HEPX, HCHs, DIEL, ENDO, PAHs, PBDEs |
| Spanish Monitoring Programme on POPs | PNA-COP | Spain | 12 EMEP sites 6 urban sites | 2008–present | Passive (PUFdisk) | PCDD/Fs, non-/monoortho-and majority PCBs, DDTs, HCB, HCH, PBDEs |
| The UK Toxic Organic Micro Pollutants (TOMPs) programme | TOMPS | UK | 6 | 1991–Present | Active/non-directional | PCDD/Fs, PCBs, PAHs |
| National Dioxins Program (Australia) | | Australia | 10 | September 2002–August 2003 | Active/non-directional | PCDD/Fs, co-planar PCBs |

*Notes*: ***** DDTs = dichlorodiphenyltrichloroethane isomers, DIEL = dieldrin, ENDO = endosulfans, PeCB =Pentachlorobenzene, HCB = hexachlorobenzene, HCHs = hexachlorocyclohexanes, HEPT = heptachlor, HEPX= heptachlor epoxide, PAHs = polycyclic aromatic hydrocarbons, PCBs = polychlorinated biphenyls, PCDD/Fs= polychlorinated dibenzo-p-dioxins and furans, PentaCB = pentachlorobenzene, PCNs = polychlorinated naphthalenes, PCP = pentachlorophenol, PFC = perfluorinated compounds.

### 2.2.3. Time Lags and Low Doses

Theoretical biology and ecosystem theory are active academic disciplines that have been working for many decades to formulate logical models to describe phenomena observed by biologists monitoring the field [23–27]. In 1977 the publication of SJ Gould s "Ontogeny and Phylogeny" [28] was a turning point in theoretical biology and ecosystem theory by, if not inventing, making good use of the concept of heterochrony that is the coexistence of multiple time frames in biological assemblages. There are patterns, sequences of events that are invariant, conserved across a number of translations and transformations of the individual units or registered events. Cellular development, embryos and evolution are turbulent, intermittent, diffusive and dissipative avalanches of eddies in a flow. "An eddy can be thought of as a typical turbulence pattern, covering a range of wavelengths, large and small eddies co-existing in the same volume of fluid. The actual modes of turbulence are eddies and high-vorticity regions, eddies can be considered as a tangle of vortex elements (or lines) that are stretched in a preferred direction by mean flow and in a random direction by another" [29]. Living processes add to the scaffold of simultaneous nested eddies, time lags and heterocronic patterns so that different eddies have, so to speak, different internal modes. These internal modes position point events by local modifications of the flow. In this sense it can be said that some eddies are also bundles, that is have an internal story that links the events inside that shielded point event with patterns and invariants that propagate in fine deviations of mass and momentum from the external flow. These fine deviations are constant and invariant in a multiplicity of point events separated in space and time. It is well understood today that flow perturbations can propagate in multiple media at different speeds as in neural cascades, metabolic pathways, genetic lineages and evolutionary trajectories [30] producing a landscape where multiple timeframes coexist.

The space time scale specificity of certain types of singularities such as molecules, organism or ecosystems can be understood as the combined result of multiple, and limited, speeds of propagation of material perturbations within and between singularities. The propagation of perturbations in different media at different speeds results in a heterochronic landscape where multiple time frames coexist in a consonance of trajectories flowing in transient bundles. Transient bundles where local regional and global process interact. A particular example of such a singularity or bundle of trajectories is a person and her/his inventory of POPs at a point in time. That inventory is the result of exposure, intake, and metabolic intrinsic degradation rates over her/his lifetime [3] and thus the current composition of a body, including its POPs burden, integrates perturbations in the environment that might have occurred decades ago originating many miles away.

It can also be argued that a person by her actions in the course of life contributes to a varying degree to the release of POPs to the environment and thus contributes to the POPs plume in the future. From the consumption of energy, agricultural and industrial products any individual is the source of a later plume as much as the composite result of the past one it has sampled. Developing models to understand better the impact of life styles and habits in the release of POPs, including product life cycle analysis, e-waste and illegal dumping shares many challenges with other international efforts in the task of monitoring and modeling releases, transport and exposure and degradation in a multiplicity of time frames and is of central importance to develop effective measures to decrease POPs in the environment.

We have briefly highlighted three issues, baselines, mixtures and time lags that we think are central in the development of further work in monitoring and modeling POPs and effective strategies to produce and share data and models. The existence of good quality data and models depends on the stable cooperation of many competent people motivated by different objectives in different institutional frameworks, geographical locations and scientific disciplines. It has been shown to be important in the development of effective international strategies to develop QA/QC procedures for monitoring work and organize regular inter comparison exercises to consolidate and maintain levels of QA/QC in the field and in the laboratory for listed monitoring programs and laboratories, including data management and access issues. The importance of keeping collections of samples for later analysis has been shown for several POPs (*i.e.*, PFOA, HBCDD) [5]. This has costs but is central to what will be a long term effort to monitor a varying number of target POPs over decades to come.

Over the past three decades science based, legally binding environmental agreements (UNECE CLRTAP) and the Montreal Protocol on Ozone Depleting Substances (M ODSs) have shown their value in terms of advancing the scientific understanding of environmental problems and designing effective strategies to deal with them. Future work should take into account that the original designs, targets and ambitions of long term programs and agreements need to be realigned inside and between them with updated knowledge that was not available at the time of planning [31].

A central component of the effectiveness evaluation is a well developed and stable strategy that can argue for the scientific and policy value resulting from an active and inclusive monitoring and modeling community of practice.

## 3. Existing Frameworks for Monitoring and Modeling LRT and Fate of POPs

For the purpose of this paper, the existing models of POPs fate in the environment can be sorted into four large groups by two basic characteristics: Are they single media (only atmosphere, ocean) or multimedia? and are they Lagrangian or Eulerian? Lagrangian models describe the evolution of the trajectories of clouds of particles in the model space, Eulerian models define a partition of the model space in compartments or boxes and describe changes inside and between the homogeneous boxes.

Early single media atmospheric LRT models were developed in the late 19th and early 20th century in the context of chemical warfare, these models were applied in the 1950s to describe the atmospheric transport of radioactive isotopes and later in 1960s to air pollution, acidification and LRT of Sulfur and acidifying substance [32–35]. These models were Lagrangian and could be solved by solving the equations with relatively little numerical computation. Until the advent of powerful computers most boundary-layer prediction methods were highly empirical and based on ordinary differential equations. The impact of computers by the mid 1960s led several workers to develop methods based on the governing partial differential equations of mean motion, incorporating turbulence transport equations [29]. When computers and programming (flow charts, *etc.*) became available to civilians after Saturn V in the 1970s the Eulerian models that cannot be “solved” analytically but can be computed numerically “in extenso” became dominant in the atmospheric modeling community. In recent years interest has been growing for Lagrangian and trajectory models.

In 1984 the European Monitoring and Assessment Programme (EMEP) was established under CLRTAP. EMEP has provided over three decades publicly available emission inventories, continental

Lagrangian and Eulerian operational transport and atmospheric chemistry models running with 6h meteorology for each year. EMEP also runs a network of some 150 air monitoring stations in Europe.

As described in [36] "*The monitoring concept established by EMEP is similar to what is serving similar monitoring efforts outside the European region, including North America (NADP, IMPROVE, CAPMoN and others), South East Asia (EANET), Africa (Debits), and South Asia (Male Declaration). These regional programs are contributing to the WMO Global Atmospheric Watch (GAW) programme. In December 2004, the EMEP Task Force on Hemispheric Transport of Air Pollution (TF HTAP) was established as a response to the increasing scientific evidence of the importance of intercontinental transport of air pollutants. Since its first meeting in June 2005, the TF HTAP has organized a series of projects and collaborative model experiments designed to advance the state-of-science related to the intercontinental transport of ozone, particulate matter, mercury, and POPs.*"

The following paragraphs provide a brief description of regional and global POPs modeling frameworks and are based on the 2010 report of the Hemispheric Transport of Air Pollution task force [4] (pp. 127–166).

Multimedia mass balance models describe the environment as a set of homogeneous boxes or compartments, each representing a specific medium, for example air, water, soil or biota. Concentrations of a chemical in each compartment are calculated by solving for each box and time step a mass balance equation that relates releases and the degradation, sequestration and inter compartment fluxes. Early multimedia mass balance models were developed in the 1970s and early 1980s, which is about a decade after the early air monitoring stations and campaigns unfolded and data were available on a few POPs [37–39]. The models were formulated using fugacity as a criterion of equilibrium of partitioning between air, water, soil and biota [40,41].

The SimpleBox model is a well known example of a multimedia mass balance model than can be applied with steady state or dynamic equations. It is a multimedia fate model that describes the environment as ten compartments at four nested spatial scales, local, regional continental and global [42]. The SimpleBox model structure has been adapted to the European Union System for the Evaluation of Substances (EUSES), a decision-support instrument which enables government authorities, research institutes and chemical companies to carry out rapid and efficient assessments of the general risks posed by chemical substances.

Many multimedia models envisage the environment as a set of spatially delimited and well mixed compartments, described by a set of constant values over an interval of time, the values are calculated from the equations at each iteration or interval, a useful and simple approximation to deal with multiple media and scale independent features of flow in organisms and ecosystems. Spatially resolved multimedia fate models have been developed since the 1990s [43,44]. A range of spatially explicit multimedia mass balance models have been based on the Berkeley-Trent (BETR) modeling framework [45–47]. Other notable spatially explicit multicompartment models are described in [46,48,49].

Multi compartment chemistry transport models are general atmospheric circulation models that include atmospheric transport and chemistry modules, extended to global multicompartment chemistry transport models (MCTM) by including in air transport models the surface compartment and parametrization or surface exchange. These models can be Lagragian or Eulerian. The Meterological Synthesizing Center East under LRTAP/EMEP has worked for two decades on such a model [50]. It is a nested three dimensional Eulerian multimedia POPs transport model. The model describes atmospheric and ocean circulation, phase transitions and degradation time within media and intermedia exchange. It has been used to estimate transboundary fluxes distinguishing primary and secondary sources of POPs.

Other multi compartment chemistry transport models in current use include MPI-MCTM [51], GEMP/POPs [52] and the Danish Eulerian Hemispheric Model (DEHM-POP).

LRT of POPs has also been studied using Lagrangian dispersion and trajectory models [53,54]. These models can be run both forward and backward in time [55] and have been successfully used to study the past distribution and fate of emissions of low-volatilty POPs from known primary sources [53]. The Lagrangian model HYSPLIT-SV has been implemented to preserve source receptor relations, which enables the ranking of source contributions to specified receptors of interest for exposure routes [53,56]. The modeling community using FLEXPART has shown to be very effective in using available monitoring data to improve knowledge on source receptor trajectories [57–59].

In evaluative applications models examine how LRT depends on different known factors included in the models such as chemical properties, weather conditions and information on releases. In simulative studies the goal is to contrast the simulation with empirical observations, and thus gauge gaps of the model with observed features and aim to advance in the understanding of POPs pathways [4] (p. 135). Intercontinental pathways for selected POPs were studied in [60].

Ocean transport is expected to be most important for persistent substances that are highly water soluble and have low vapor pressure and Henry’s Law constant [4]. Perfluorinated acids are a relatively new class of persistent pollutants that have these characteristics. The global transport of perfluorinated acids in oceans has been modeled in simulative studies [61–64]. Together, these studies demonstrate that oceanic transport of persistent and hydrophilic substances can result in substantial transfer to remote ecosystems such as the Arctic Ocean.

Air-sea exchange of semi-volatile substances allows for multiple cycles through the atmosphere and ocean [4] (pp. 198–205). Oceanic transport enhances long-term meridional transport, as relatively fast currents exist along some continents (Africa and the Americas). Net northward transports prevail in the Northern Hemisphere oceans [51,65]. On the other hand, transfer of contaminants from surface waters to the deep sea by both deep water formation and sinking with sedimentation of particulate matter (biological pump) [66,67] may slow down long-range transport and modulate a contaminant’s mobility. In addition, the biological pump can decrease the contaminant atmospheric levels even in polar regions or the earth due to sequestration of atmospheric POPs by enhanced air-water diffusive fluxes driven by phytoplankton uptake and organic carbon settling fluxes [67]. These processes should be taken into account in future monitoring in order to better interpret available data on atmospheric concentrations.

### *3.1. Challenges in Evaluating Current Levels and Changes over Time*

#### 3.1.1. Releases, Emissions Source Receptor and Reverse Modeling

As it has been noted above, POPs present specific problems due to the fact that they can be released from products and these are transported over long distances from production to use to disposal, can be deposited on water or soil and be re-emitted after deposition. Consequently, to estimate emissions, more details are needed than for other pollutants. Furthermore given the large number of substances concerned complete inventories of all substances are not and will be not available. A number of efforts have been undertaken and have delivered the best available estimates for very few substances (e.g., a-HCH, PCB-28, PCB-153) [50,51]. A vast effort is underway under the SC in cooperation with UNEP to develop methods and inventories of unintentional emission of POPs (e.g., PCDD/F) and Article 6 on National implementation plans and Article 15 on reporting expect parties to calculate and report estimates of their emission for all POPs.

Monitoring data can help to improve understanding source receptor relations in two ways: (1) in the context of models that use emission estimates, based on activity levels of different sectors and emission factors. Emission estimates are used as input in direct models of transport that estimate atmospheric concentrations or deposition fluxes, the calculated values can be compared with monitoring data. By changing the emissions, source receptor relations can be investigated. Alternatively (2) in the context of Lagrangian air mass back trajectory models (e.g., FLEXPART, HYSPLIT) that simulate flow backwards in time and space indicating the origin of air masses sampled at a given site [57–59]. Motoring data and reverse modeling can be used to estimate the intensity of sources identified in space and avoid to large extent the always difficult emission estimates to advance in the understanding of current levels and pathways.

The international cooperative efforts working on the deployment of passive air samplers [4,21,22] have significantly improved the regional and global coverage in space and time of monitoring data for POPs in air. In this context, reverse modeling can certainly be an effective tool to develop a better understanding of current release baselines and changes over time [46]. This is important for the EE of the SC and the attribution of observed changes in concentrations to measures undertaken, or other processes.

### 3.1.2. Time Lags, Dynamic Responses, Mixtures, Low Doses

Part of the difficulty in dealing with non steady state, dynamic responses and time lags come from the hypotheses of homogeneity, and instantaneous propagation embedded in the physical and chemical models of environmental pathways. The models assume inside the boxes that represent gas, liquid and solid media the properties of the medium are scale invariant, homogeneous and change simultaneously for the whole compartment.

One might ask here, how can ecosystem models help improve modeling POPs? and how could POPs models help ecosystem modeling? and a tentative answer is precisely in monitoring and modeling scale dependent features while keeping a view of the multimedia and multiscale nested nature of the processes.

Models in ecology apply different types of enumeration rules that identify monitored or modeled registered points and track the trajectory bundles in models of molecules, cells, multicellular organism and their skeletons and shelters, modes of foraging, reproduction, and dispersal in populations, lineages and ecosystems interacting in evolutionary games. These enumeration rules, made explicit in taxonomic or demographic frameworks, identify individuals and changes over space and time. Several kinds of models are applied to describe and predict dynamic features in biological assemblages. These include scale invariant models of the basic thermodynamic and stochiometric constraints in living pathways where autotrophic organisms, by photosynthesis or chemosythesis produce reduced carbon—carbon bonds, these energy rich bonds oxidized in the presence of oxygen and other electron acceptors release the metabolic energy that drives all biological flows. The net result of carbon inputs and losses in a system over a particular time (Net Ecosystem Carbon Balance), is intermittent and in words of Burke and Lauenroth [68] "The distribution of all biologically active elements can be explained by the fact that they are bonded to carbon skeletons and travel through the biota in concert with carbon. Thus the rate at which carbon skeletons are formed and broken controls element cycling. Reiners [69] described two major categories of organic compounds, protoplasmatic and mechanical, which have distinct element ratios. For instance, protoplasmatic compounds (enzymes, nucleic acids, *etc*.) have high concentration of nitrogen, while mechanical or structural components (wood, bone, shell) have higher concentrations of materials that are resistant to decay (e.g., lignin) which tend to accumulate in soils and sediments. Thus when the net carbon balance is positive, biologically active elements are stored, and when it is negative, they are released to inorganic forms, leaving them vulnerable to movement through gaseous or soluble form or being bound in mineral form".

The net carbon balance or net primary production in biological assemblages identified as: cells, multicellular assemblages or individuals, geographically dispersed populations, and ecosystems is intermittent at all scales. Recurrently short positive phases where foraging, reproduction and dispersal occur are followed by long phases where the accumulated materials are mixed back to the inorganic mineral pool. The development of multicellular organisms, colonies, microbial mats, canopies and other ecosystem structures are linked to the reproduction of these distinct time frames related to multimedia phase transitions.

One could envisage a model of populations (an array of registered point events) where the classic model of population dynamics tracking numbers of discrete individuals reproducing feeding and dying is replaced by models including transient bundles of converging and diverging trajectories (molecules, cells, organisms, ecosystems) in a cascade of nested Lagrangians. In this sense then for a number of scale ranges one can describe an external Lagrangian (e.g., trajectories in an air mass) and internal Lagrangians (e.g., trajectories in a pollen grain travelling for a while in that air mass). In the future one could imagine multimedia nested Lagrangian models of transport (MNLs) describing trajectory bundles over a range of coordinates in space, time and phase space at different scales including time lags and grain in ways that Eulerian box models can hardly do.

Time lags that are clearly relevant for current POPs modeling work include the long time it can take for a molecule to travel from its first release in to a free moving medium through a long multimedia trajectory to exposure, where it becomes part of the body of an organism. These time lags in the environment are mediated by the interaction of air with other media such as water, soil and sediment. Inside an organism a complicated hetero chronic landscape of flows and degradation rates integrate a long term exposure history into an instantaneous effective dose that might elicit negative effects. The consequences of those effects in turn can take long time, even several generations, to amplify or be perceptible.

A somewhat different but related kind of time lag that is relevant here are policy formulation and implementation time lags. Over the past decades from the early pesticide and PCB controls in the late 1970s, it has repeatedly been the case that it takes less than a decade to identify a problem (*i.e.*, a globally present artificial toxic) it takes three to four decades to agree and implement measures and in many cases (e.g., DDTs, PCBs, HCHs) it takes a few years to see the results in remote locations. A better use of monitoring and modeling could eventually decrease this pathetic 30–40 year time lag that has of course significant public health and environmental consequences and costs.

Important issues when considering POPs monitoring and modeling are that (a) very low levels in the environment over time can yield significant exposures and harmful effective doses and thus need to be accurately measured and (b) any sample contains a complex mixture of POPs [5]. This translates into stringent QA/QC constraints in the analytical, data management and modeling work, that in turn makes POPs research very valuable as scientific and technical precursor. It can be argued that Radiation Protection from the 1940s to the 1960s contributed many of the tools, such as mass spectrometers, and concepts such as exposure, dose, effective dose, ecosystem pathways and LRT models that are in use today for many other environmental issues. POPs work today is, in a sense, a continuation of that effort in the context of contemporary knowledge of molecular, genetic, endocrine and ecosystem processes.

### 3.1.3. Monitoring, Modeling and QA/ QC for Effectiveness and Science

Monitoring and modeling have shown in recent decades to be at the base of successful environmental policies on a global scale such as LRTAP [31,36] and, Montreal Protocol on Ozone depleting substances (M ODSs) [70]. The efforts developed under large scale environmental agreements have also shown to be productive in scientific and academic terms. But there are still major hurdles and things that can be improved. For instance “data waste”, and the lack of visibility or credit for the monitoring work. Regarding, the waste of data, it is clear that vast amounts of good quality monitoring data, intermittent measurements or short time monitoring studies are not used to the extent they could be used because there is no motivation, procedure or location to make them available and useful for other users. On the second issue it is clear that better use can be made of existing data and tools to increase awareness of scientist, policy makers and general population of the utility, relevance and interest of environmental monitoring and modeling. Effective monitoring and modeling of POPs requires long chains in space and time of dedicated professionals striving to keep and demonstrate QA/QC standards and to share data and compare results. Developing respect and giving credit to the weakest elements in these chains is in the long term very important.

We have briefly reviewed theoretical and practical tools that are used for monitoring and modeling POPs in the environment, these tools exist and are used by individuals in the field, the laboratory or other location. As we have noted above when a quantitative statement is made about the environment (e.g., this sample contains 20 pg of PCB28) a number of events are taking place at the same time in multiple space time frames. Some of these events are very short term and local like the prevailing wind and the screws at the station when the sample was taken, or when the value is published in some report. Other frames are linked with the past and the future, embedded in the tools, the methods the expertise, and the communication lines, that make those measurements meaningful data, useful and trustworthy for other people.

The work with the sample in the field, in the laboratory and the overall imaginary construction in which the individual worker performs her or his work have a social, anthropological and political dimensions [10,71–73]. Institutional arrangements and work plans provide the background where productive research and policy initiatives can unfold, a framework for collective learning trajectories, where useful knowledge is produced and shared.

## 4. Monitoring and Effectiveness Evaluation Strategies under the SC, LRTAP and M ODSs

In recent decades a number of initiatives focused on building science based policy instruments for protecting public health and the environment from pollutants have established international agreements and procedures. The work under these agreements has clearly been effective in increasing available knowledge on the issues and in number of cases (LRTAP, M ODSs, SC) provided fertile fields to establish scientific cooperation and reciprocal capacity building across disciplines and regions of the world. These efforts have implemented public health, environmental protection and air quality policies that can be shown to have been effective. It is possible for instance to simulate what the atmospheric load of ODSs and the stratospheric Ozone hole would be today if control strategies had not been implemented 20 years ago [74]. It is consequently relevant to identify and consolidate the conditions for existence of effective long term institutional arrangements and work plans that have shown to yield results in line with their objectives.

### *4.1. The Stockholm Convention*

The SC includes several articles that indicate the engagement of parties to cooperate in monitoring and modeling among others, Article 7, Implementation plans, Article 8 Listing of Chemicals, Article 10 Public information, awareness and education, Article 11 Research, development and monitoring, Article 15 Reporting and Article 16 Effectiveness evaluation. This last article reflects the ambition of parties to develop a process to evaluate the effectiveness of the Convention. In order to facilitate such evaluation it established (2004) arrangements to provide comparable monitoring data on the presence of the chemicals listed in the convention as well as their regional and environmental transport under the Global Monitoring Plan (GMP). The conference of the parties also established (2009) a working group that developed a framework and a number of process and outcome indicators to carry out the effectiveness evaluation (EE) and identify ways to improve the effectiveness of the Convention as a whole. The draft EE framework was presented to the Conference of the Parties in 2011. The revised EE framework was adopted in 2013.

The EE primary objective is to identify if concentrations of POPs are decreasing in core media air and human tissue (milk and blood). The secondary objective is to attribute those changes, when possible, to identifiable causes, and ultimately based on this information identify actions that could improve the effectiveness of the SC.

The GMP has established a number of strategic partnerships with long term stable monitoring processes with well established QA/QC for the core media. For air these have included AMAP, LRTAP EMEP, NCP, IADN, TOMPS, GAPS, MONET among others (see Table 1 for the programs that contributed to the 2009 GMP report) and for human samples WHO, UNEP, AMAP, CDC, GerES, ESB among others [4,20]. In 2009 the GMP presented the first global report and in 2013 published the updated version of the guidance document that includes technical guidance for monitoring and reporting data on all listed POPs in all core media. This document will be the base for the 2015 global report.

The EE framework adopted by the parties in 2013 states in paragraph 25: “To reduce data limitations it is important to increase the comparability of long-term global monitoring data in the core media and to provide support for developing countries and countries with economies in transition to participate in monitoring activities to address the gaps identified in the global monitoring plan report.” This has been addressed trough a number of programs under UNEP, AMAP and other organizations. The adoption of passive air samplers in recent years has significantly improved air monitoring and provides a wealth of data to improve fate and transport models [7,21,22].

The EE framework of the SC is based on the assessment of three streams of information, monitoring data and assessments provided by the GMP, information on what actions and work plans countries have reported in their National Implementation Plans and Article 15 reports, and information from the Compliance procedure, that aims at facilitating the compliance by parties with their obligations under the treaty. The Compliance procedures are still under discussion and thus this information is not available yet.

The focus of the EE is to enhance and improve the effectiveness of the convention as a whole. This implies establishing agreed baselines, observing changes over time with agreed data and methods and working on the attribution of the observed changes in a modeling community of practice.

Two aspects have to be mentioned here in the context of facilitating the implementation of the SC EE. First the interest and advantage of enhancing the integration of GMP monitoring and modeling with global efforts (GAW&GEO, IGBP) and second the evolution from and learning of existing successful hemispheric and global monitoring and modeling efforts such as LRTAP and M ODSs.

On the first aspect the WMO GEO work is a good base including the GEO 2012-2015 Work Plan [75], in particular Task HE-02 on “Tracking Pollutants” and its component on “Global Monitoring of Persistent Organic Pollutants” [76]. Enhancing cooperation of GMP with GAW and GEOSS would be positive for GMP data providers and data users as well as making GMP work available for people dealing with other related issues.

### *4.2. The UNECE Long Range Transboundary Air Pollution Convention*

The synergies between the CLRTAP and the SC have a long history and play a central role in the implementation of both Conventions. The monitoring and modeling community that has matured under the CLRTAP could benefit from the SC expertise with POPs for the implementation of its POPs protocol in ECE countries and beyond and the SC could benefit from the networks, databases and methods of work CLRTAP has implemented over three decades to advance in its monitoring and modeling. In particular, EMEP/EBAS, HTAP and the Working Group on Effects [77]. Several of these elements implemented in the CLRTAP have been central in the development of EU air monitoring and modeling to develop air quality strategies and also for the SC. The specific environmental behavior of POPs preclude the use of the standard impact models used in CLRTAP and new concepts have to be developed. The emission/transport /exposure/impact logic and many of its operational components have provided and do provide a good base for work on the effectiveness of POPs work.

### *4.3. The Montreal Protocol on Ozone Depleting Substances*

The Vienna Convention for the Protection of the Ozone Layer and its Montreal Protocol on Substances that Deplete the Ozone Layer [78] dedicated to the protection of the earth's ozone layer are certainly a paradigmatic success story in environmental science and policy. Aa very large problem, the depletion of ozone in the stratosphere was identified and swiftly attributed to a very small number of artificial substances produced by a handful of companies. A vast effort was deployed to understand, monitor and try to control the problem. With 197 parties, it is the most widely ratified treaty in United Nations history, and has, to date, enabled reductions of over 97% of all global consumption of controlled ozone depleting substances (measured in ozone depletion potential (ODP) tonnes). The Parties to the Montreal Protocol are informed by three panels of experts on the effectiveness of the measures undertaken, the Scientific Assessment Panel (SAP), the Environmental Effects Assessment Panel (EEAP) and the Technology and Economic Assessment Panel (TEAP). The three panels produce a detailed report every four years, the most recent SAP report was published in 2010. The executive summary of the 2010 Scientific Assessment integrating the information from the three panels provides an excellent overview of the quality and interest of the work produced under the arrangements of the Montreal protocol.

It has been recognized since the 1970s that a number of compounds emitted by human activities deplete stratospheric ozone. The Montreal Protocol on Substances that Deplete the Ozone Layer was adopted in 1987 to protect global ozone and, consequently, protect life from increased ultraviolet (UV) radiation at Earth's surface. Chlorine- and bromine-containing substances that are controlled by the Montreal Protocol are known as ozone-depleting substances (ODSs). ODSs are responsible for the depletion of stratospheric ozone observed in polar regions (for example, the "ozone hole" above Antarctica) and in middle latitudes. The severe depletion of stratospheric ozone observed in the Antarctic has increased UV at the surface and affected climate at southern high latitudes.

The Montreal Protocol and its Amendments and Adjustments have successfully controlled the global production and consumption of ODSs over the last two decades, and the atmospheric abundances of nearly all major ODSs that were initially controlled are declining. Nevertheless, ozone depletion will continue for many more decades because several key ODSs last a long time in the atmosphere after emissions end [79,80].

There are important differences between the problems posed by ODSs and POPs. ODSs are present primarily in the atmosphere, while POPs are distributed in all media. Short-term quantifiable effects of the reduction of ODSs such as the volume of the ozone layer and UV radiation can be observed, while it is very difficult to quantify effects on ecosystems and health effects of POPs mixtures over time. The later point being one of the reasons for the special importance of the precautionary principle to operate the SC properly.

Many of the monitoring and modeling challenges addressed in the context of ODSs, such as the multiplicity of process involved, time lags and potential confounding factors as well as what is done in the context of this Protocol to deal with these issues are a place to learn for the the design of monitoring and assessment tools to evaluate and enhance the effectiveness of the SC.

One outstanding element described in the 2010 Scientific Assessment of the M ODSs is the significant impact of the Montreal Protocol on Green House Gases concentration in the atmosphere:

"The Montreal Protocol and its amendments and adjustments have made large contributions toward reducing global greenhouse gas emissions. In 2010, the decrease of annual ODSs emissions under the Montreal Protocol is estimated to be about 10 gigatonnes of avoided CO2-equivalent emissions per year, which is about five times larger than the annual emissions reduction target for the first commitment period (2008–2012) of the Kyoto Protocol."

These two agreements (LRTAP and M ODSs) have deployed a very effective institutional framework and work plan over a number of decades integrating monitoring and modeling to evaluate the effectiveness of the measures undertaken. Their experience is not immediately transportable to the SC due to multiple reasons, but there are a number of potential synergies and commonalities in theory and practice that we have tried to describe.

## 5. Closing Remarks

POPs are a public health and environmental problem and POPs are also good tracers of pathways and flows. Tracing POPs pathways through monitoring and modeling is important to deal with the problem their presence poses. Tracing POPs helps in advancing the understanding of atmospheric and oceanic long range transport, as well as ecosystem and organism scale biological process and flows.

The distributed process of monitoring and modeling POPs in the environment is based on the agreement of registration rules specified in field and in laboratory methods, instruments, taxonomies, and calendars. The use of these collectively developed institutions and rules produces registered point events that are then published or otherwise made available for data analysis and modeling. A multiplicity of academic disciplines and their respective enumeration rules of registered point events and trajectories are relevant for POPs, from molecular biology to atmospheric physics, many processes documented by data and models interact and need to be traced to formulate predictions and plan observations and measures [81]. A more effective logical and institutional integration of monitoring and modeling environmental pathways is possible and would be useful. This needs to be envisaged in the context of significant changes in the available tools to store, handle and share models and data [82–84].

Many new tools for work in the field and the laboratory are being developed and this will continue. In general they provide easier, more accurate and cheaper results. At the same time the move towards "open science" and "open data" and the development of visualization tools that can be used by the public will define the communication of science and the implementation of the SC.

From a theoretical perspective we suggest that some form of multimedia nested Lagrangian model of trajectory bundles in a turbulent flow could be helpful in exploring the interplay of scale invariant and scale dependent processes relevant to understand time lags and the impact of mixtures and low doses.

From a practical point of view we note that many valuable monitoring data on POPs are wasted and that better use of available data of POPs in the environment could result of developing procedures to credit, in academic and professionally effective terms, researchers who deposit detailed and documented data in public supervised data warehouses that can then be used for further research. We envisage a distributed network of data hubs that makes best use of analytical and computational innovations and provides open access services. The maintenance of such facilities relies on the existence of long term international agreements and a persuasive public demonstration that high quality monitoring data are necessary to develop effective public health and environmental strategies.

The GMP under the SC EE framework establishes a long term process that can help to approach these objectives.

Monitoring an modeling POPs does not make any sense in isolation and much attention should be paid to potential synergies and co benefits resulting from a better integration across academic disciplines and environmental initiatives to improve transport and fate models. This integration can advance constructing better links between scale invariant multimedia multi substance models of fluid dynamics and scale dependent biological models of cells organisms and ecosystem pathways. It is also important to further develop monitoring and modeling in view of emerging scientific issues, such as the biogeochemical modulation of air chemistry in polar regions and the changing pathways and transformation rates in the environment, that were not on view in earlier stages of research.

We think it is important to underline the need to develop multiscale and multimedia models able to deal with the multiplicity of modes of propagation and interaction that can translate into long time lags between emission and exposure, exposure and effect. Having a better understanding of these time lags is central to evaluate and improve the effectiveness of policy measures undertaken to decrease the risk to humans and the environment from contaminants such as POPs. Multimedia nested Lagrangian models could provide useful insights into the bundles of trajectories that modulate the chemical landscape from cells to ecosystems.

## Disclaimer

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## Conflicts of Interest

The authors declare no conflict of interest.

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