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Toward the Next Generation of Air Quality Monitoring: Persistent Organic Pollutants (POPs)

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HIGHLIGHTS

- Global air monitoring of POPs should provide consistent and comparable data.
- Emission can be used to assess regional environmental performance concerning POPs.
- Using air measurements, reverse-modeling can be used to estimate emissions.

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ABSTRACT

Persistent Organic Pollutants (POPs) are global pollutants that can migrate over long distances and bioaccumulate through food webs, posing health risks to wildlife and humans. Multilateral environmental agreements, such as the Stockholm Convention on POPs, were enacted to identify POPs and establish the conditions to control their release, production and use. A Global Monitoring Plan was initiated under the Stockholm Convention calling for POP monitoring in air as a core medium; however long temporal trends (>10 years) of atmospheric POPs are only available at a few selected sites. Spatial coverage of air monitoring for POPs has recently significantly improved with the introduction and advancement of passive air samplers. Here, we review the status of air monitoring and modeling activities and note major uncertainties in data comparability, deficiencies of air monitoring and modeling in urban and alpine areas, and lack of emission inventories for most POPs. A vision for an internationally-integrated *strategic monitoring plan* is proposed which could provide consistent and comparable monitoring data for POPs supported and supplemented by global and regional transport models. Key recommendations include developing expertise in all aspects of air monitoring to ensure data comparability and consistency; partnering with existing air quality and meteorological networks to leverage synergies; facilitating data sharing with international data archives; and expanding spatial coverage with passive air samplers. Enhancing research on the stability of particle-bound chemicals is needed to assess exposure and deposition in urban areas, and to elucidate long-range transport. Conducting targeted measurement campaigns in specific source areas would enhance regional models which can be extrapolated to similar regions to estimate emissions. Ultimately, reverse-modeling combined with air measurements can be used to derive "emission" as an indicator to assess environmental performance with respect to POPs on the country, region, or global level.

1. Introduction and objective

Persistent Organic Pollutants (POPs) are an international concern due to their resistance to degradation, ability to be transported over long distances from sources by air and ocean currents, and potential to bioaccumulate through terrestrial and aquatic food

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webs to levels that may result in adverse health effects for animals and humans. Due to these concerns, multilateral environmental agreements (MEAs) have been enacted to control the release, production and use of POPs, including global conventions dealing with toxics and waste (the Basel and Rotterdam Conventions), the Stockholm Convention (SC) on POPs, and the POPs Protocol under the United Nations Economic Commission for Europe (UNECE) Convention on Long-Range Transboundary Air Pollution (CLRTAP).

Air is the major route of long-range transport through the environment for many POPs (UNEP, 2009, 2013). In areas where there are no sources of POPs, atmospheric transport drives contaminant levels. Thus, both SC and CLRTAP have provided frameworks to monitor POPs in the atmosphere. These include the Global Monitoring Plan (GMP) for SC (which has identified air as one of the two core media for monitoring), the European Monitoring and Evaluation Programme (EMEP) and the Working Group on Effects (WGE) for CLRTAP. Various national and regional monitoring programs, and surveillance-type studies, provide valuable data on POP concentrations in air. However, standard environmental indicators for POPs to interpret these concentrations and to assist in policy-making are still lacking (UNEP, 2012).

The objective of this article is to propose a systematic structure for collecting and applying information about the atmospheric concentrations of POPs, in order to develop and evaluate potential indicator(s) for assessing environmental performance at curtailing POPs at national, regional and global scales. Such indicators could be incorporated into the Environmental Performance Index (EPI), which ranks countries according to how close they are to established environmental policy goals (http://epi.yale.edu/).

Our approach is to first identify gaps and deficiencies in the existing ambient air monitoring and measurements for POPs by assessing spatial coverage, temporal resolution and measurement techniques. We then develop a vision for a *strategic monitoring plan* that integrates measurements and modeling, and would provide an empirical basis to develop standard air quality indicators for both short- and long-term environmental performance assessments.

The development of air quality indicators for POPs presents significant challenges distinct from other priority air pollutants due to several specific characteristics:

(1) Health impacts of POPs are not immediate; and usually result from chronic, cumulative, and long-term exposure to one or more substances. For example, POPs do not usually cause respiratory health effects.
(2) POPs can partition to multiple environmental media (air, soil, water, sediment, plants, animals etc.) and the major exposure route is non-atmospheric; e.g. through ingestion and bioaccumulation. For many POPs, the atmosphere serves as an entry-point into the environment where they are carried from sources to receptors.
(3) Sources of POPs vary spatially and temporally depending on use and transport. Primary emission sources may be agricultural [for organochlorine pesticides (OCPs)], industrial [polychlorinated biphenyls (PCBs), poly- and perfluorinated compounds (PFCs), flame retardants (FRs)], health-related applications [dichlorodiphenyltrichloroethanes (DDTs) and lindane], or unintentional releases due to combustion [polychlorinated dibenzo-*p*-dioxins/furans (PCDD/Fs) and polycyclic aromatic hydrocarbons (PAHs)]. As atmospheric concentrations of legacy POPs decline, reservoirs that have accumulated in oceans, land and snow/ice can become 'secondary sources' that re-emit POPs to the atmosphere. The profile of POPs in air at any given location is unique; representing a combination of local and regional primary and secondary emissions coupled with transport from more distant regions mainly through air but also via water or even biovectors (e.g. migrating birds, fish, marine mammals).
(4) Toxic effects of POPs manifest themselves in multiple endpoints and are not well defined for mixtures of POPs. Some endpoints may not even be recognized yet.
(5) There are sampling and analytical challenges for POPs due to their very low ambient air concentrations [typically in pg m^{-3} (1 ppq) or lower], and the large number and variety of POPs. Real-time analysis of POPs is not yet feasible with existing instrument sensitivity.
(6) New POPs are continually being added to national and international control initiatives (Scheringer et al., 2012). In many cases, there are high uncertainties regarding the physico-chemical properties and environmental fate and behavior of these new substances. The increasing number of POPs presents resource (including financial) and technical challenges for existing monitoring programs.

Recently, several extensive assessments have identified the deficiencies in the air monitoring and measurements of POPs, and made recommendations for improvements, including UNEP (2007, 2012, 2013), UNECE (2010) Part C, and AMAP (2010). Viewpoint articles (e.g. Klánová et al., 2011) and special issues in the peer-reviewed literature have also addressed the role of science in supporting international efforts to regulate and monitor POPs [*Atmospheric Pollution Research* vol.3 (4), 2012 and *Trends in Analytical Chemistry* vol. 46, 2013]. Here, we summarize and build on the information given in these documents and translate them into a form that is usable by decision-makers for developing indicators specifically for POPs.

2. Overview of Current monitoring systems, modeling and indicators

2.1. Current monitoring networks and sampling techniques

Two main types of air sample collection techniques are used for POPs: active sampling (involving pulling air through a trap with an electric pump, e.g. high- or low-volume air sampling) and passive air sampling (PAS) (mainly diffusion-based, trapping chemicals on sorbents without the use of electricity). Concentrations of POPs in air derived from these two techniques are not always directly comparable; but they complement each other by providing different information. Active sampling provides quantitative concentrations of POPs in both gas and particle phases over short time intervals (several hours to 1 week) whereas PAS provides semi-quantitative data over longer periods (typically 1–3 months up to 1 year) (Harner et al., 2004; Wania et al., 2003). Recent developments include a passive flowthrough sampler (FTS) that captures both gas and particle phase chemicals in relatively large-volume air samples for use in remote locations (e.g. the Arctic and the Tibetan Plateau) (Xiao et al., 2007, 2012). Active sampling is more expensive to operate, more labor intensive and requires power, therefore it is well-suited for intensive monitoring at well-equipped stations. PAS is cheaper, easy to deploy and, thus, better-suited for remote monitoring sites or for developing a large network of sites. More information can be found in UNECE (2010) and UNEP (2013).

Fig. 1 shows a map of currently-operating monitoring sites and networks. Most networks using active sampling techniques started in the 1990s (circles in Fig. 1) and those using PASs started in the mid to late-2000s (squares in Fig. 1). Sampling sites that were previously in operation and may be restarted to assess concentration changes, are given in Fig. A1. Additional network information can be found in UNECE (2010). Following the establishment

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