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Measurement and Modeling of Atmosphere-Surface Exchangeable Pollutants (ASEPs) To Better Understand their Environmental Cycling and Planetary Boundaries

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Rockström et al.[1] warned that to avoid "unacceptable global change" humanity must operate within nine planetary boundaries, including one associated with chemical pollution. Diamond et al.[2] concluded that implicit in the concept of a safe operating space for chemical pollution is a finite global assimilative capacity for chemical pollution defined as the ability of an ecosystem to render a substance harmless, that is, to avoid adverse effects. We suggest that measurement and modeling of the fate and transport of toxic compounds that disseminate globally through repeated cycles of atmosphere-surface exchange should be incorporated into efforts to identify safe boundaries and integrate those boundaries into systems of governance.

Compounds that disseminate by atmosphere-surface exchange are those that can be classified as "hoppers" and "multiple hoppers" in Wania's[3] chemical property space. Wania distinguished pollutant groups according to regions of a diagram of $\log_{10}$ of air−water equilibrium partition coefficient, log K_{AW}, vs $\log_{10}$ of octanol−air equilibrium partition coefficient, log K_{OA} (Figure 1), labeling them as fliers, swimmers, single hoppers, and multiple hoppers on the basis of their partitioning and degradation behavior. Included in this set of substances are numerous polychlorinated biphenyl (PCB) compounds, polycyclic aromatic hydrocarbons (PAHs), pesticides, and other, but not all, persistent organic pollutants (POPs). Mercury (log $K_{OA\_Hg(0)}$ = 1.1) can also be viewed as an atmosphere-surface exchangeable pollutant (ASEP).

Because of their persistence and semivolatility, ASEPs are prone to global dissemination (so governance requires regulation and management on a global scale), but ASEP impacts are most acute at the local scale (where management of ASEPs is often not possible). The mismatch (both spatially and temporally) between pollutant source and impacts often leads to disproportionate impacts on marginalized communities, particularly Indigenous communities with a strong traditional reliance on freshwater or marine food sources. For example, certain pesticides and PCBs threaten the food sources of Indigenous peoples in the Arctic despite little or no history of uses of these chemicals in the region. A mismatch also exists when one country requires mercury controls on power plants, but increasing coal combustion without controls in other countries results in mercury continuing to be a concern in the former. These local impacts by global sources of ASEPs can be addressed only by multijurisdictional approaches to governance as exemplified by the Stockholm and Minamata Conventions.

We argue that the "planetary boundary" associated with an ASEP should include a time component. By definition, *persistent* pollutants have a significant atmospheric lifetime, but the tendency of ASEPs to cycle between mobile (atmosphere, ocean) and more stationary (land, lake or ocean sediments) environmental reservoirs lengthens the period of active cycling in the environment. The residence

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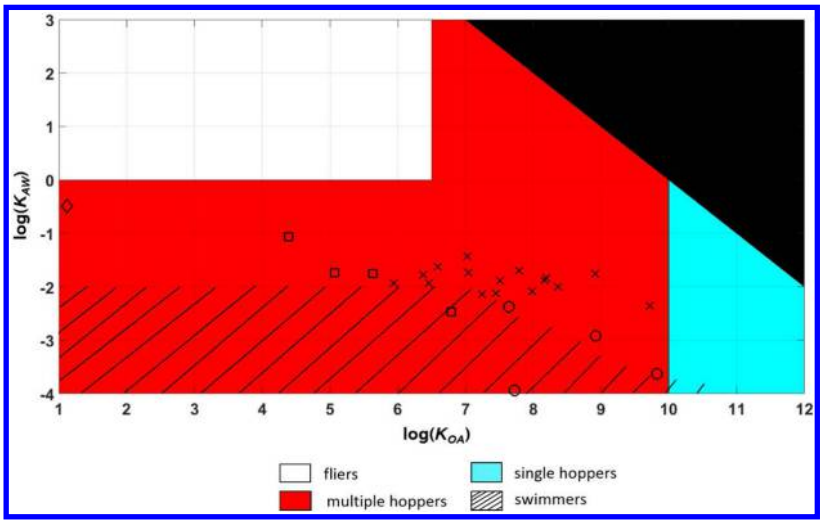

Figure 1. Major modes of environmental transport of hypothetical perfectly persistent pollutants (see legend) and actual pollutants (atmospheric half-life >2 days; half-life in surface media >0.1 year): mercury (◊), PCBs (×), pesticides (○), and PAHs (□). Graphics modified from ref 3 with permission. Copyright 2006 the American Chemical Society.

time of a PCB congener in the water column of a lake is typically weeks to months, but once the sediments are considered together with the water column, the residence time can expand to decades. As a result, toxic effects are felt for prolonged periods and long after restrictions are placed on primary emissions. For example, atmospheric deposition of PCBs to North America's Lake Superior has been decreasing since the 1970s, but PCB concentrations in Lake Superior fish have been stable since the mid-1990s. Therefore, if emissions are not regulated until after harmful effects are observed, the associated harmful effects can persist or even increase for decades. Timely regulation, or when feasible a preventative strategy, is thus important for this class of compounds, and measurements that lead to more accurate modeling can help determine the consequences of delay and the benefits of swift response.

Assessing the effectiveness of international efforts to reduce global emissions of ASEPs (as required for POPs by the Stockholm Convention) or planning emissions reductions to achieve desired environmental outcomes is best informed by an iterative process of comparing model-predicted environmental concentrations with monitored concentrations and model improvement. Once model improvements enable more accurate understanding of the drivers of current environmental concentrations or the historical trend in those concentrations, then emissions reductions required to achieve desired environmental concentrations can be informed by the models. Current protocols have established monitoring networks such as the Arctic Monitoring Program (AMAP), Great Lakes Integrated Atmospheric Deposition Network (IADN), and the European Monitoring and Evaluation Programme (EMEP). Monitoring results by themselves cannot tell us the degree of emissions reductions required. A requirement for iterations of model predictions and model improvements is not routinely incorporated into international agreements to regulate ASEPs.

Model improvements are needed to better understand the sources and sinks of contaminant in the environment, to evaluate effects of interacting stressors (e.g., climate change, land use change), and to suggest policy options for reducing contaminants. The major environmental sink for many ASEPs is burial (sequestration) in soils and sediments. A complex interplay of climate, biology, and land cover determines the extent of ASEP uptake by vs re-emission from terrestrial surfaces.[4] Rates of this removal process are impacted by human land-use and climate change. Sequestration of ASEPs is an environmental service provided by organic matter storage in soils, wetlands and sediment. Policies that enhance sequestration, based on sound models, are an alternative to policies that call for emissions reductions.

Improvements in models of the fate and transport of ASEPs require measurements to elucidate mechanisms of transport and transformation. Measurements across environmental gradients of the most uncertain ASEP processes, for example atmosphere-surface exchange,[5] sequestration, and effects of land use on these two processes, are needed. The measurements should drive improvements in model parametrizations of these processes. It is also necessary to develop more accurate inventories of current and forecasted primary emissions and re-emissions for various policy scenarios, and to integrate those inventories into chemical fate and transport models. Selection of policies needed to reduce primary emissions and re-emissions to the required level in the desired time frame is facilitated if models can predict the efficacy of the policies.

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Notes

The authors declare no competing financial interest.

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