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Past, Present, and Future Controls on Levels of Persistent Organic Pollutants in the Global Environment

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Understanding the legacy of persistent organic pollutants requires studying the transition from primary to secondary source control.


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Under the Stockholm Convention, signatory countries are legally required to eliminate production, use, and emissions of persistent organic pollutants (POPs), with the goal of reducing human and ecosystem exposure. Available data and models indicate that atmospheric levels of the most well-studied legacy POPs, especially polychlorinated biphenyls (PCBs), hexachlorobenzene (HCB), and dichlorodiphenyltrichloroethanes (DDTs) are declining slowly in Europe, North America, and the Arctic (*1*−*3*). This decline is believed to primarily reflect the actions taken internationally over the last two decades to reduce or eliminate major primary sources associated with production and use. However, there are still ongoing primary releases from diffuse sources that are difficult to target for reduction or elimination, such as volatilization from old stockpiles, or from old equipment that is still in use (*4*).

Understanding and predicting the past, current, and future trends of POPs in the environment requires that we account for both primary emissions and re-emissions to the atmosphere from reservoirs in the global environment. These "secondary sources" are soils, vegetation, water bodies, and, indirectly, sediments that were contaminated in the past when primary emissions were much higher. Net re-emission from these environmental media is triggered by declining atmospheric concentrations and controlled mainly by temperature and biogeochemical processes.

Secondary sources can be viewed as "capacitors" that were charged with pollutants deposited from the atmosphere when levels were higher, and which may now be net sources of POPs to the atmosphere. Further progress in reduction of primary emissions of POPs may not be directly reflected in atmospheric levels because secondary sources will buffer the decline of atmospheric concentrations that would otherwise be expected. In fact, secondary sources already potentially represent a significant fraction of the total source inventory, especially in remote areas.

The current balance between primary and secondary sources in determining global exposure to POPs is not easy to assess because rates of both types of emission remain highly uncertain. Inventories of primary emissions are difficult to assemble and factors controlling re-emission from secondary sources are variable and not yet fully understood. However, we believe that the principal control on the levels of "classical" POPs in active circulation in the global environment is currently in a state of transition. It is clear that primary sources dictated levels in the past, especially during the initial period of increasing production, use, and emissions. And it is equally clear that in the future, secondary sources will be dominant because primary sources will ultimately be eliminated. When this is achieved biogeochemical factors will be the main drivers controlling the distribution, depletion/degradation, and extent of human and wildlife exposure to the burden of these POPs in the environment (*5*). This transition from primary to secondary source control may take many decades. During this time, environmental exposure to POPs is controlled by a dynamic balance between these two driving forces.

The biogeochemical controls on the fate of POPs have so far been quantitatively addressed mainly using global scale fate models (*6, 7*), and only a few experimental studies (i.e., refs *8*−*10)*. The models and experiments both indicate that organic carbon (OC) and the carbon cycle play a key role in influencing the fate of POPs. In general, POPs are moderately volatile and hydrophobic, and thus have a tendency to partition from air and water into organic phases. The biogeochemical cycles of POPs and OC may therefore be linked in various ways, as illustrated in Figure 1 for PCB 153 (a hexachlorinated biphenyl compound). Fluxes and budgets for PCB 153 and OC were extracted from calculated global scale mass balances (*11*−*17*). Both of these global mass balances are highly uncertain, and in some cases no estimate of fluxes, in particular for POPs, are possible. Such an assessment shows that in the year 2000, the equivalent of about 50% of the total annual anthropogenic emission of PCB 153 was cotransported to the storage compartment (soil or sediments) associated with the different pathways of OC. The high degree of coupling between OC and POPs is empirically evident in the vertical distribution of POPs in undisturbed soils and sediments, which behave as a record of the historical POP emissions (*10*).

In a secondary source controlled world, OC pools will represent the major active stores and sources of pollutants. Under these conditions, prediction of exposure is not dependent on knowledge of primary use, but rather on understanding the influence of biogeochemical processes, particularly those surrounding the global mass balance of carbon. Important processes in the OC cycle, such as burial/storage in terrestrial subsurface layers during organic carbon transformation, riverine export in dissolved and particulate form, and export of particle-bound chemicals by settling to deep sediments are expected to represent the main pathways driving the incorporation of POP into the reservoirs and POP exposure for uptake in biota. The challenge is 2-fold since we must understand both the anthropogenic (e.g., changes in land use) and the natural factors that control re-emission of pollutants from OC rich secondary sources.

Clearly, the biogeochemical fate of carbon is intimately associated with the spectre of global climate change. Forecast changes in climate (e.g., temperature, precipitation amount, and intensity), land disturbance, and the deposition of nutrients (*18*) will affect ecological processes, altering photosynthetic and respiratory C fluxes and possibly the magnitude of the C sinks (i.e., net loss of OC). Changing hydrological condition(s) also usually lead to concomitant changes in lateral dissolved organic carbon (DOC) transport from catchments to surface waters due to changes in flowpath, while a near doubling of DOC concentrations in surface waters in some parts of the northern hemisphere over the last two decades has been linked to a reduction in acid deposition (*18*). Additionally, any increase in soil erosion will increase the export of C in particulate form to aquatic systems. In marine environments, too, changing physical conditions have been observed to disrupt trophic food webs, altering the net ecosystem exchange of C (*19*). The question here is, can these processes influence the strength of the environmental sinks for POPs or even result in a net release of old burdens of POPs from C rich reservoirs?

Prediction of future POP exposure scenarios therefore requires a cross-field fertilization, implying a closer cooperation between the POP and the C-cycle research communities. We suggest this occurs in two main areas:

a. Coupling POP Distribution, Partitioning, and Reactions in Terrestrial and Aquatic Systems to OC Distributions, Pools/Fractions, and Turnover

Some recent studies are already making inroads here by estimating the dynamic coupling of air and forest systems (*20*) and air−phytoplankton systems (*21*), where biologically driven cycles can act to "draw down" atmospheric loadings of POPs and remove them from the atmosphere into forest soil C pools and the deep oceans. These studies quantify the mass of POP associated with the active C pool over time (e.g., through a growing season) in order to address the strength of the sink for atmospheric pollutants. Hence, there is a clear need to further improve our understanding of the fate of POPs within the environmental capacitors. Current models fail to describe the complexity of the interaction between POP fate and incorporation and turnover of organic matter in soils and surface waters. For example,

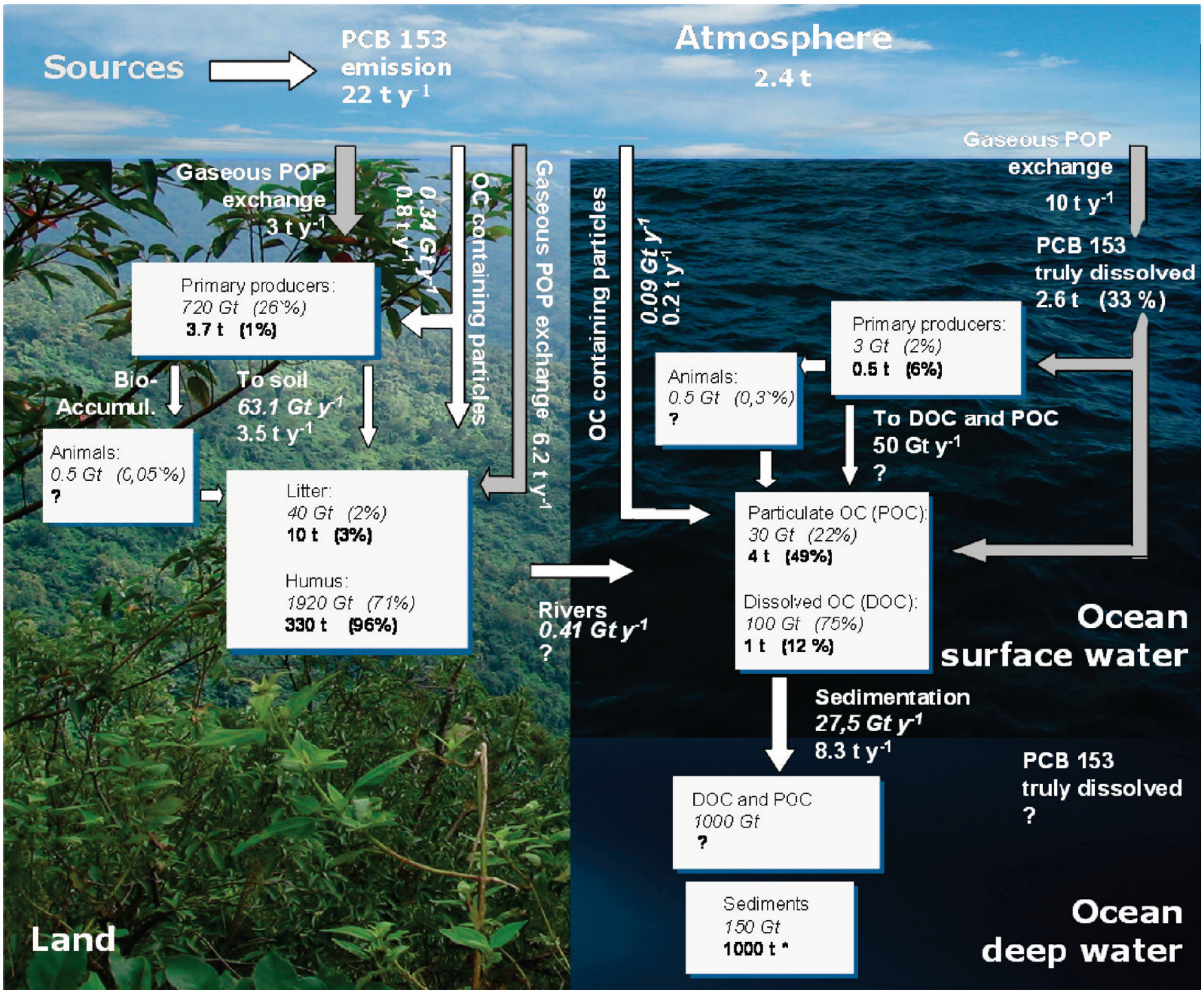

FIGURE 1. Environmental burden of PCB 153 associated with the major C pools and its intercompartment cotransport in association with OC (white arrows). Gray arrows represent the net passive exchange of PCB 153 from the gas phase in the atmosphere or the truly dissolved phase in water to the OC reservoirs. Data are reported in bold for PCB 153 and in italics for OC. Flux data are in white; pool data are in black. Numbers in parentheses refer to the percentage of PCB 153 and OC in a given compartment in relation to the total compartment inventory. Fluxes and inventories for PCB 153 were extracted from the mass balance obtained using a global multimedia fate model (*11*) and from ref *47*. Unsteady state simulation was performed by assuming the historical high emission scenario to the atmosphere of PCB 153 from ref *4* and results are calculated for year 2000. Pools and fluxes of OC are from refs *12*–*17*, *48*. Disappearance processes for PCB 153 and OC are not represented in the figure. Loss fluxes (e.g., due to degradation and respiration) are not represented. Note: * indicates estimated from ref *49*.

in soil ecosystems little progress has been made in developing a mechanistic description of biodegradation processes from the perspective of their ecological drivers. Research into the ecology of the "unseen majority" (*22*), i.e., the microbial communities, as major degraders and/or processors of environmental chemicals, is required. In particular, specific emphasis on community structure–function relationships and microbial adaptations to climate change is necessary. Of particular relevance here is the understanding of the mechanisms and system properties controlling bioconcentration and bioavailability of POPs (*23*). Recent achievements in this area shed some light on unexpected fungus–bacteria interactions controlling the kinetics of POP degradation (*24*). Furthermore, only very few studies have focused on POP transfer processes in soils at the microscale (*25, 26*), for example, by analyzing the partitioning of pollutants to different fractions of the soil organic and inorganic matrix. In the aquatic ecosystem, investigation of the coupling between OC pools and fate of POPs has been carried out mainly through measurement of POP partitioning between water and size-fractioned plankton (*27, 28*) or between water and OC in sediments (*29*). This approach provides a rough and static picture of such coupling. Unfortunately, given the lack of appropriate experimental tools to conduct observations, the description of the dependence of POP fate on the dynamics of synthesis and turnover of OC rarely evolves beyond the phase of model assessment (*30, 31*).

Animals too may represent a non-negligible fraction of the total OC stored in the biosphere. Within POP research, accumulation in trophic food webs has been the focus of many studies, mainly in connection with understanding ecological processes and biota/human exposure assessment. On the other hand, very little is known on the potential quantitative role of the animal biosphere in influencing distribution and processing of the environmental burden of POPs. As the total biomass diminishes rapidly for each energy transfer in the food web, one may perhaps assume that animal biomass has little influence on global POP distribution. However, most recalcitrant POPs are retained up the food web with an efficiency that approximately counterbalances the decrease in total biomass (*32*). Thus, although the total amount of POPs at higher trophic levels may be comparable to that present in the "standing crop" at the base of the food web, the concentrations are much higher due to the reduced biomass and the slower turn over. If the burden of POPs in animals is not negligible relative to the total environmental burden, then animals' potential roles as "biovectors", "biotransformers", and "bioreservoirs" must be considered.

Due to habitat use and migration on various scales, animals contribute to POP transport as "biovectors" on a local scale (e.g., from marine to freshwater systems (*33*); from sea surface layers to seafloor (*34*)); on a long-range scale (e.g., migration to remote areas from populated overwintering areas (*35*)); and facilitate redistribution of POPs between media (e.g., bioturbation and biotransfer from sediment to water (*36*) or mixing of superficial soil layers (*37*)), with the likely effect of influencing overall fluxes of POPs between storage and transport compartments. As species distribution in the environment shifts with climate in the future, as already seen in displacement of large fisheries, global distribution of POPs due to animal habitat use and migration is also likely to shift.

Many POPs interact with animal physiology and may be acted upon by enzymatic systems, in which the parent compound is "biotransformed" to a different chemical species. Although biotransformation results, on the one hand, in net loss of parent POPs from the ecosystem, on the other hand it may result in the formation of new compounds such as the metabolic products oxychlordane and hydroxy-PCBs that are either retained in the body or excreted to the environment (*32*).

Broadly speaking, the life span of organisms increases up the trophic food web, and with increased life span, the animals may function as "bioreservoirs" the comparison of burden per compartment may not be applicable because the biomass turnover rate of each trophic level is very different and must therefore be considered. For example, in the aquatic system, the standing crop of primary producers may not be larger than that of zooplankton, but the turnover rate of phytoplankton can be several times faster, resulting in an integrated larger biomass.

Assessment of the role of animals in influencing the fate of POPs at the global scale is made difficult due to a lack of knowledge regarding the global biomass of different trophic levels. To carry out a proper evaluation, a dynamic perspective should be incorporated in which a thorough ecological understanding of species and key processes is reflected.

b. Need for a Step-Change Improvement in Air−Surface Flux Measurements of POPs to Investigate the Mechanisms of POP Re-Emissions from Environmental Stocks

We believe that the implementation of micrometeorological techniques in POP air−surface exchange flux measurement is necessary to fulfill the knowledge demand on the coupling between C and pollutant cycles, especially in ecosystem based studies. This approach should be used, initially, to carry out a finer mechanistic investigation of the processes controlling POP deposition to and re-emission from environmental capacitors, enabling higher accuracy in the quantification of transport at a variety of spatiotemporal scales. Additionally, it will allow systematic detection of diffuse, primary, and secondary sources, thereby contributing to the further development of source inventories and the estimation of emission factors. Such measurements should also provide earth science researchers with useful tracers for the further development of understanding of biogeochemical and physical processes.

The necessary tools, techniques, and infrastructure needed are those already used to understand global CO_2 air−surface exchange and water and energy budgets. The introduction of micrometeorological techniques in the early 1980s in the study of gaseous ecosystem exchange (*38, 39*), together with the availability of highly sensitive detectors, has provided ecologists with a direct means to measure CO_2, water vapor, and energy fluxes. Nowadays, micrometeorological flux measurements are routine and represent the basic experimental platform for ecosystem exchange studies (*40*).

In contrast, POPs environmental transport research has been hampered by lack of suitably sensitive analytic methods leading to poor spatiotemporal resolution of flux observations. Online, real-time detection of airborne POPs has not been possible due to the large air volumes required to exceed limits of detection. Higher frequency observations of gaseous concentration as required for micrometeorological flux measurement techniques has also been hindered by the expense and time required for solvent-based sample extraction.

Although micrometeorological measurement of POP fluxes has been implemented in a number of studies in the presence of strong sources (e.g., agricultural fields after pesticide application (*41*), or heavily contaminated soils (*42*)), recent improvements in sampling and analytic technology have enabled these measurements to be conducted in background conditions and with greater precision even on moving platforms such as ships (*43*). Accumulative approaches such as gradient techniques or relaxed eddy accumulation currently represent the best means to measure POP air−surface exchange fluxes. New sampling devices and analytic techniques have been developed that enable phase separation and ultratrace concentration measurement to be performed following short sampling times (*44*−*46*). This development is essential in order to fulfill the requirement of stationary atmospheric conditions necessary for implementing micrometeorological flux measurement. The new sampling/analysis technology also allows considerable reduction of analytical time and cost.

We believe that the two areas of cross-field fertilization outlined are relevant for the development of the POP field to fulfill the requirements of the present and future knowledge demands. Their implementation will provide environmental managers with the information required to assess the effectiveness of current mitigation practices, and to further develop policies to govern the transition toward new stages of POP management.

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