Oceanic Biogeochemical Controls on Global Dynamics of Persistent Organic Pollutants

JORDI DACHS, *† RAINER LOHMANN, † WENDY A. OCKENDEN, ‡ LAURENCE MEJANELLE, ‡ STEVEN J. EISENREICH, § AND KEVIN C. JONES ‡

Department of Environmental Chemistry, IIGAB-CSIC, Jordi Girona 18-24, Barcelona 08034, Catalunya, Spain, Environmental Sciences Department, Lancaster University, Lancaster, LA1 4YN, UK, Laboratory of Marine Chemistry and Biogeochemistry, University of Paris VI, Paris, France, and Institute for Environment and Sustainability, Joint Research Centre, Ispra (VA) 21020, Italy

Understanding and quantifying the global dynamics and sinks of persistent organic pollutants (POPs) is important to assess their environmental impact and fate. Air-surface exchange processes, where temperature plays a central role in controlling volatilization and deposition, are of key importance in controlling global POP dynamics. The present study is an assessment of the role of oceanic biogeochemical processes, notably phytoplankton uptake and vertical fluxes of particles, on the global dynamics of POPs. Field measurements of atmospheric polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), and furans (PCDFs) are combined with remote sensing estimations of oceanic temperature, wind speed, and chlorophyll, to model the interactions between air-water exchange, phytoplankton uptake, and export of organic matter and POPs out of the mixed surface ocean layer. Deposition is enhanced in the mid-high latitudes and is driven by sinking marine particulate matter, rather than by a cold condensation effect. However, the relative contribution of the biological pump is a function of the physical-chemical properties of POPs. It is concluded that oceanic biogeochemical processes play a critical role in controlling the global dynamics and the ultimate sink of POPs.

Introduction

The long-range transport, persistence, and global dynamics of persistent organic pollutants (POPs) have been issues of increasing concern during the past decade, because they are key to understanding the potential impact of POPs on ecosystems, human health, and their ultimate fate (1–9). The United Nations organized several international conferences, leading to the UNECE POPs protocol (10). International protocols require criteria for assessing the environmental risk associated with POPs, that can only be provided by sound scientific knowledge, data, and models. Present knowledge of the global dynamics of POPs is incomplete. Further effort is therefore needed to understand the mobility and the processes controlling the ultimate global sinks of POPs.

Some of the issues concerning the global distribution and dynamics of POPs that have received particular attention are the potential for persistence and long-range transport (2, 4, 11), Wania, Mackay, and collaborators (1, 12–14) developed a model with several climatic zones that has been used to study the accumulation of some POPs, such as γ-HCH, in arctic regions. This model suggests that temperature plays an important role in controlling transport and sinks at the global scale through the processes of cold condensation, global distillation, and latitudinal fractionation. This interesting approach has triggered most of the studies on long-range transport during the past decade. Experimental evidence for global fractionation and cold condensation has been observed in terrestrial and limnic systems but is scarce in the marine environment (6, 15, 16–18). However, these limited data suggest that these processes may be of relatively minor importance, compared to other processes affecting the fate of POPs, such as sorption to organic matter, sequestration in deep waters, etc. (18–20).

Long-range atmospheric transport between different regions of the world could occur as a sequence of successive volatilization and condensation processes, a process called the “grasshopper effect” (1). These small steps are strongly influenced by diurnal and seasonal variability of environmental conditions, such as temperature, due to its influence on air-surface partitioning. Air–water exchange has been shown to dominate depositional processes to many aquatic systems for a wide range of POPs such as PCBs and HCHs (19). In marine environments, POPs sorb to particulate organic matter and a fraction of it may eventually sink to deep waters and sediments (20–22). Once POPs are sequestered by sinking particles, they will be effectively removed from participating in dynamic air–water exchange. Settling fluxes of POPs in the water column can therefore be considered to represent a final sink controlling the surface recycling, impact and sinks of POPs. However, the role of sinking particles and other biogeochemical processes, such as phytoplankton uptake, on the global dynamics of POPs has so far not been assessed.

Recently, it has been shown that phytoplankton uptake and air–water exchange behave as coupled processes in aquatic environments (23). First, air–water exchange supports phytoplankton concentrations of POPs in atmospherically driven aquatic environments, and second, trophic status influences the magnitude of air–water exchange (24). Indeed, eutrophic conditions lead to a depletion of water column concentrations, due to phytoplankton uptake and settling export (24, 25). The objectives of this study are to determine the role of biogeochemical processes, such as phytoplankton uptake and vertical fluxes of particles, on the global dynamics of POPs and to assess their importance, relative to other processes such as air–water exchange. This study is based on field measurements of PCBs and PCDD/Fs, remote sensing estimation of oceanic temperature, wind speed and chlorophyll, and modeling of the interactions between air–water exchange, phytoplankton uptake and export out of the mixed layer of POPs scavenged by particulate organic matter.

Field Measurements and Data Sources

POPs Data Sets. Field measurements of atmospheric concentrations of PCBs and PCDD/Fs were made during a North-
South Atlantic Ocean transect (52°N–72°S) during the fall (October–December) of 1998. Full details of the cruise route, sampling, and analytical procedures are given elsewhere (26, 27).

Remote Sensing and Climatological Data. To study the spatial variability of the air–water mass transfer rate around the globe, global distributions of temperature and wind speed obtained by remote sensing from satellites have been utilized. Temperature may be estimated from satellite by the use of image radiometry that measures infrared radiation. The use of dual radiometers enables correction for the atmospheric influence on sea surface emitted radiation. Sea surface temperatures (SST) were obtained from the Along Track Scanning Radiometer (ATSR) installed in the European Space Agency ERS-2 satellite (ATSR project web page, www.atsr.rl.ac.uk). SST images consist of monthly averaged data with a resolution of a half degree (360 × 720 pixels). Wind speed may be measured from satellites by the special sensor microwave/imager (SSMI). Sea surface wind speeds were obtained from the SSMI installed on the DMSP satellite of the U.S. government (NOAA web page, http:// orbit-net.nesdis.noaa.gov). Sea surface wind speed is averaged monthly with a resolution of 1 degree (180 × 360 pixels). Chlorophyll concentrations may be used to estimate the spatial distribution of phytoplankton biomass at the global scale. Chlorophyll concentrations are estimated from fluorescence signals obtained from the SEAWIFS satellite (28). Mixed surface layer depth can be obtained from the Levitus climatological data with a spatial resolution of one degree.

The present study is based on monthly averages of SST, wind speed, and chlorophyll a concentrations corresponding to the sampling period of the experimental data (October–December 1998), i.e., satellite-derived variables of October 1998 were selected for the latitude range of samples taken during that month, remote sensed data from November 1998 were then chosen for the latitudes sampled in November, etc. Even though the temperature and chlorophyll distributions used are with a resolution of half degree, the limiting spatial resolution of one degree is given by the wind speed distributions.

Results and Discussion

PCB and PCDD/Fs Database. The gas-phase PCB concentrations measured in the Atlantic Ocean transect ranged from 54 to 1290 pg m⁻³ (sum of 38 congeners) and averaged 501 pg m⁻³. These concentrations are slightly higher but within a factor of 2 than those measured previously in the open Atlantic ocean by Iwata et al. (290 pg m⁻³ (9)) and in other oceanic environments (9). The measured concentrations are also within a factor of 3 to those measured in Bermudas by Knap et al. (29) and in the Canary Islands by Van Drooge et al. (191 pg m⁻³, sum of 14 congeners (7)). However, gas-phase concentrations measured over land may not be representative of what is occurring over the oceans since gas-phase concentrations are influenced by air–vegetation, air–soil, and air–water exchange (19, 31). These processes may be responsible of the higher atmospheric concentrations over ocean than over land, but further research is needed on land–ocean interactions affecting POP occurrence. Concerning the spatial distribution along the north–south transect, the more hydrophobic POPs showed higher concentrations at low latitudes than at mid to high latitudes, and higher concentrations at the northern hemisphere, consistent with emission distribution. The less chlorinated PCBs did not show such a decrease in concentrations at high latitudes but displayed uniform atmospheric concentrations over the Atlantic Ocean. Further information on the PCDD/F and PCB database used can be found elsewhere (26, 27).

Oceanic Atmospheric Depositional Processes. After long-range atmospheric transport, POPs may be deposited to the open ocean by three processes; diffusive air–water exchange, dry particle deposition, and wet deposition (Figure 1). As far as PCBs are concerned, diffusive air–water exchange is the dominant air to water depositional process (19, 32), which supports dissolved and phytoplankton concentrations in aquatic environments (24). Wet and dry particle deposition is not as important as diffusive air–water exchange, except in rainy regions and close to urban areas with high concentrations of atmospheric particulate matter (33), and for chemicals that have a strong affinity to aerosols such as polycyclic aromatic hydrocarbons (8, 31).

Air–Water Exchange. Air–water exchange may be treated in the traditional manner where the air–water flux (Fₘₜₐₜ, ng m⁻² d⁻¹) is given by

$$ F_{AW} = k_{AW} \frac{C_A}{H} - C_W $$

where C_A and C_W are the dissolved and gas-phase POP concentrations (ng m⁻³), respectively, H is the temperature corrected and dimensionless Henry’s law constant, and k_{AW} is the air–water mass transfer rate (m d⁻¹). k_{AW} may be estimated as the result of transfer through two layers at each side of the air–water interface

$$ \frac{1}{k_{AW}} = \frac{1}{k_{A,H_2O}} + \frac{1}{k_W} $$

where k_A and k_W are the POP mass transfer coefficients (m d⁻¹) in the air and water films, respectively. k_A may be calculated from the mass transfer coefficient of CO₂ in the water side (k_{AW,CO₂}, m d⁻¹), which is a function of wind speed at 10 m height (U₁₀, m s⁻¹) (34)

$$ k_{AW,CO₂} = 0.24U₁₀^2 + 0.061U₁₀ $$

$$ k_W = k_{AW,CO₂} \left( \frac{S_{POP}}{600} \right)^{-0.5} $$

where S_{POP} is the Schmidt number of the POP and 600 accounts for the Schmidt number of CO₂ at 298 K, respectively. Similarly, k_A may be estimated from the mass transfer coefficient of H₂O in the air side (k_{AW,H₂O}, m d⁻¹) that is also dependent on the wind speed

$$ k_{AW,H₂O} = 0.2U₁₀ + 0.3 $$

$$ k_A = k_{AW,H₂O} \left( \frac{D_{POP,a}}{D_{H₂O,a}} \right)^{0.61} $$

where 0.61 and 0.61 are the diffusivity coefficients of the POP and H₂O in air, respectively. From eqs 3–6, it is obvious
that wind speed has a great influence on the magnitude of $k_{AW}$. On the other hand, temperature influences the magnitude of $k_{AW}$ through its influence on diffusivities, Schmidt numbers, and $H'$. It has been suggested that temperature plays a major role on the latitudinal variability of air–water fluxes. Since the dimensionless $H'$ depends on temperature, the low temperatures at high latitudes would result in a low value of $H'$, thus leading to a higher value of the first term in the air–water concentrations gradient as given by eq 1. However, the value of the air–water fluxes also depend on $k_{AW}$, $C_W$, and $C_A$. The global distribution of $k_{AW}$ values for a given chemical can be estimated by applying eqs 2–6 to sea surface temperature and wind speed determined by remote sensing (see Methods section). Since wind speed estimations by remote sensing are monthly averages, it is important to account for the short-term variability and nonlinear influence of wind speed on $k_{AW}$. Indeed, it is well-known that short periods of high wind speed account for most of the time-integrated flux. The nonlinear influence of wind speed has been taken into account by assuming an oceanic Weibull distribution of wind speed with a shape parameter of 2 and by modifying $k_{AW}$ values as described elsewhere (35–38).

Figure 2A shows the global spatial distribution and latitudinal profile of $k_{AW}$ for PCB 52. Areas with faster air–water exchange (higher values of $k_{AW}$) are those that have both high

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**FIGURE 2.** Global spatial variability and latitudinal profiles predicted for PCB 52 in the parameters (A) $k_{AW}$, (B) $k_{WP}$, and (C) $k_{Sink}$.  

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TABLE 1. Latitudinal Variability of Temperature (T), Wind Speed (U10), Chlorophyll Concentrations (Chl), Mixed Layer Depths (MLD), and Sinking Fluxes of Organic Carbon (FOC) during the Fall of 1998a

<table>
<thead>
<tr>
<th>Latitude</th>
<th>T (K)</th>
<th>U10 (m s⁻¹)</th>
<th>Chl (mg m⁻²)</th>
<th>MLD (m)</th>
<th>FOC (mg m⁻² d⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75–90 N</td>
<td>274 (272–278)</td>
<td>10 (9–14)</td>
<td>na</td>
<td>8 (1–54)</td>
<td>na</td>
</tr>
<tr>
<td>60–75 N</td>
<td>277 (272–286)</td>
<td>10 (8–15)</td>
<td>1.5 (0.3–21)</td>
<td>26 (1–245)</td>
<td>131 (52–690)</td>
</tr>
<tr>
<td>45–60 N</td>
<td>282 (273–293)</td>
<td>10 (5–14)</td>
<td>1.3 (0.3–60)</td>
<td>28 (1–104)</td>
<td>117 (46–888)</td>
</tr>
<tr>
<td>30–45 N</td>
<td>293 (277–301)</td>
<td>8 (5–10)</td>
<td>0.5 (0.1–42)</td>
<td>29 (2–84)</td>
<td>46 (12–546)</td>
</tr>
<tr>
<td>15–30 N</td>
<td>299 (287–305)</td>
<td>7 (4–10)</td>
<td>0.3 (0.1–15)</td>
<td>33 (1–65)</td>
<td>32 (10–734)</td>
</tr>
<tr>
<td>0–15 N</td>
<td>301 (294–304)</td>
<td>8 (4–10)</td>
<td>0.3 (0.05–27)</td>
<td>24 (1–107)</td>
<td>37 (9–1005)</td>
</tr>
<tr>
<td>0–15 S</td>
<td>300 (290–305)</td>
<td>7 (3–10)</td>
<td>0.2 (0.04–18)</td>
<td>34 (1–152)</td>
<td>33 (9–377)</td>
</tr>
<tr>
<td>15–30 S</td>
<td>297 (285–304)</td>
<td>7 (4–10)</td>
<td>0.1 (0.06–1)</td>
<td>35 (3–185)</td>
<td>20 (4–499)</td>
</tr>
<tr>
<td>30–45 S</td>
<td>289 (278–298)</td>
<td>7 (4–13)</td>
<td>0.3 (0.02–14)</td>
<td>59 (1–858)</td>
<td>41 (3–1057)</td>
</tr>
<tr>
<td>45–60 S</td>
<td>278 (272–287)</td>
<td>11 (5–15)</td>
<td>0.4 (0.1–6)</td>
<td>138 (1–852)</td>
<td>54 (20–528)</td>
</tr>
<tr>
<td>60–75 S</td>
<td>273 (272–278)</td>
<td>7 (5–14)</td>
<td>0.8 (0.1–18)</td>
<td>38 (4–456)</td>
<td>89 (21–1068)</td>
</tr>
<tr>
<td>75–90 S</td>
<td>273 (272–274)</td>
<td>9 (5–14)</td>
<td>2.6 (0.2–7)</td>
<td>40 (9–205)</td>
<td>273 (31–611)</td>
</tr>
</tbody>
</table>

a Average and range (in brackets) is for all the oceanic basins.

temperatures and high wind speeds, such as the subtropical areas. The latitudinal profile of kaw shows the maxima in these regions and relatively low values at mid-high latitudes due to lower temperatures. It is important to mention that the values of kaw at mid-high latitudes would be even lower if the average wind speed were not as high as 10–11 ms⁻¹ (Table 1). It is also noteworthy to observe the opposite influence of temperature on air–water exchange, depending on whether H* or kaw are considered. Indeed, the low temperatures at mid-high latitudes will result in kaw values that would tend to limit air–water fluxes of POPs. On the other hand, low temperatures also decrease H* values in a counteracting influence on air–water exchange (eq 1). Therefore, the resulting influence of temperature on air–water exchange fluxes will depend on whether kaw has a stronger dependence on temperature than H*. Obviously, the actual air–water flux depends on the POP concentrations in water and air as well as H* and kaw. Therefore, the concentration gradient or second term in eq 1 will also exert an important control on air–water fluxes. As demonstrated in remote lakes, the Great Lakes region of North America, and in coastal environments (23–24, 39), the concentration gradient is influenced by biogeochemical processes such as phytoplankton uptake and sinking fluxes of particles. To assess the influence of these processes in the ocean, we need first to determine the global distribution of the mass transfer coefficients for water–phytoplankton exchange and the sinking fluxes of POPs.

**Water–Phytoplankton Exchange.** Once pollutants enter the oceanic surface mixed layer, they sorb to phytoplankton and a fraction will sink associated to phytoplankton cells, fecal pellets, and other aggregates (20–22, 40) (Figure 1). Fluxes of POPs between water and plankton (F_wp, ng m⁻² d⁻¹) are given by eq 7

\[ F_{wp} = k_{wp} \left( C_w - \frac{K_{wp}}{K_{cp}} C_{wp} \right) \]  

(7)

where \( C_p \) is the POP concentration in phytoplankton (ng kg⁻¹), and \( k_u \) (m² kg⁻¹ d⁻¹) is the uptake and depuration rate constants, respectively; \( k_{wp} \) (m d⁻¹), the mass transfer coefficient between water and plankton, depends on the mixed layer depth (MLD, m), the phytoplankton biomass (\( B_p \), kg m⁻³), and the uptake constant (23).

\[ k_{wp} = \text{MLD} \times B_p \times k_u \]  

(8)

\( k_{wp} \) values were estimated from eq 8 using the Levitus MLD climatological values, \( k_u \) values reported elsewhere (23, 41), and phytoplankton biomass estimated from chlorophyll concentrations as determined by remote sensing techniques (28). Figure 2B shows the predicted global variability and latitudinal profiles of \( k_{wp} \) for PCB 52. \( k_{wp} \) increases at mid and high latitudes due to the high phytoplankton biomass in these areas and to the deep MLD in the Southern Ocean during the period of time considered. \( k_{wp} \) values also increase for more hydrophobic POPs, due to the linear dependence on \( \log K_a \) on log \( K_{OM} \) values (41). Phytoplankton uptake is a two-compartment process with adsorption to the phytoplankton cells also being important for some POPs (21, 41, 42). This process is also described by an equation analogous to eq 7 but with adsorption (\( k_{ads} \), m² kg⁻¹ d⁻¹) and desorption \( (k_{des}, \text{d}^{-1}) \) rate constants instead of \( k_u \) and \( k_{wp} \). The water–phytoplankton surface transfer rate \( (k_{WPS}, \text{m d}^{-1}) \) thus depends on \( k_{ads} \). However, adsorption onto the cell surface is always faster than absorption into the cell, thus it will never be the limiting step in the sequestration of POPs to the deep ocean.

**Sinking Fluxes.** Vertical fluxes of particle-associated POPs are lacking in most multimedia models, probably because it is a nonfugacity driven process. However this is a key process needed to understand the oceanic sinks of POPs, and an estimation of the global distribution of vertical fluxes of POPs is presented here for the first time. Vertical fluxes of POPs out of the mixed-layer are given by the product of POP concentrations in sinking particles to the vertical flux of sinking organic matter \( (F_{SOM}, \text{ng m}^{-2} \text{ d}^{-1}) \). To compare these fluxes with those of air–water and water–phytoplankton exchange, sinking fluxes can be parametrized by eqs 9 and 10.

\[ F_{sink} = k_{sink} \times C_{p} / K_{u} \]  

(9)

\[ k_{sink} = F_{OM} / K_{d} \]  

(10)

where \( k_{sink} \) (m d⁻¹) is the mass transfer rate coefficient for sinking of POPs. Similar to the discussion above for water–phytoplankton exchange, an analogous equation to eq 9 should be used to account for the sinking of adsorbed POPs which will depend on a second transfer rate \( (k_{strs}) \). The major problem in estimating the global variability of \( k_{sink} \) by applying eq 10 comes from the availability of \( F_{OM} \) values at the global scale. Several methods exist for the estimation of \( F_{OM} \) from primary productivity and chlorophyll concentrations which have been summarized elsewhere (43). Fluxes estimated by these different methods and integrated over the various oceanic basins do not differ by more than 30%, except in the Arctic ocean where results from different prediction methods are disparate (43). In the present work the sinking flux of
organic carbon \( (F_{OC}, \text{mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}) \) has been estimated using the correlation reported by Baines et al. (44)

\[
\log(F_{OC}) = 2.09 + 0.81 \cdot \log(\text{Chl})
\]

where Chi is the chlorophyll concentration (mg m\(^{-3}\)) as determined by remote sensing (see methods). \( F_{OC} \) is estimated by multiplying \( F_{OC} \) by 1.8 (45) and is used to calculate \( k_{sink} \) values according to eq 10. Latitudinal profiles and the global predicted variability of \( k_{sink} \) for PCB 52 are shown in Figure 2C. Due to the log–log relationship between \( F_{OC} \) and Chi, \( k_{sink} \) values follow the spatial variability of chlorophyll concentrations, thus showing higher \( k_{sink} \) values at mid-high latitudes and in upwelling areas. Sinking velocities will be higher for the more hydrophobic POPs, due to the dependence of \( k_{sink} \) on the ratio \( k_{A}/k_{S} \).

**Air–Deep Oceanic Water Transport.** The present approach divides the oceanic waters into two distinct compartments, the surface mixed layer and the “deep oceanic waters”. The air–deep water exchange may be considered as the result of three important processes in series: air–water exchange, water–phytoplankton exchange, and particle sinking (Figure 1). Air–water and water–phytoplankton exchange are reversible processes and thus POPs transfer from air to phytoplankton and from phytoplankton to air. However, the sinking particle flux is a one-way loss process and therefore is the final sink of POPs to deep oceanic waters. The quantification of the ocean as a sink is important to understand the long-term behavior and impact of POPs. On a long-term basis and due to the persistence of these chemicals, we can assume that the air–water–plankton–deep water transport is in steady state over the time scale of the present study. Therefore, the fluxes between air and water equal the fluxes between water and plankton and they equal the sinking fluxes

\[
F_{AW} = F_{WP} = F_{Sink}
\]

The system of eqs 1, 7, 9, and 12 can be solved to provide estimations of the global variability of \( C_{W}, C_{P}, \) and \( F_{Sink} \) provided that the atmospheric concentrations of POPs are known. In the present work we assume that the atmospheric concentrations of PCBs, PCDDs, and PCDFs measured for a certain latitude at the Atlantic Ocean are representative of the atmospheric concentrations at the same latitude in all the oceans. Obviously, this is a gross simplification, as POPs concentrations vary spatially and temporally; nevertheless, these assumption allow illustrative estimations to be derived. Figures 3A and 4A show the oceanic gas-phase concentrations of PCB 52 and PCB180 derived from the measured concentrations over the Atlantic ocean (26, 27).

Predicted global distributions and latitudinal profiles of \( C_{W} \) and \( F_{Sink} \) are also shown in Figures 3 and 4 for PCB 52 and PCB180, respectively. Predicted \( C_{W} \) values show high variability at a given latitude, even though the corresponding gas-phase concentrations are assumed to be constant. This is the result of the spatial variability of physical and environmental conditions, such as wind speed, phytoplankton biomass, etc., which affect the occurrence of POPs in the water column. Evidence of the important role of biogeochemical processes on the occurrence and fate of POPs is stressed in the upwelling regions. Upwelling areas are regions of high chlorophyll concentrations and, therefore, of high sinking rates. For example, in the area off-shore of the Sahara, Peru, Namibia, or in the Arabian Sea, a predicted depletion of dissolved phase concentrations of POPs is observed. The more hydrophobic the chemical the more apparent is this phenomenon as illustrated for PCB 180 (see Figure 4). The low concentrations of dissolved POPs in the mixed layer of high primary productivity regions are driven by enhanced sinking fluxes of particle associated POPs that cannot be supported by the air–water diffusive inputs from the atmosphere. This phenomenon has been demonstrated and reported before for remote lakes in Canada, and for Lake Ontario (21, 23) and the present results suggest that it also plays an important role in oceanic waters. As far as the latitudinal profiles of dissolved phase POPs are concerned, they follow the gas-phase POP concentrations to a certain extent but are influenced by physical and biogeochemical variables such as temperature and phytoplankton biomass. The relative influence of these variables depends on the physical-chemical properties of the chemical as demonstrated in the following section.

The predicted sinking fluxes, which are equal to the air–water exchange fluxes, due to the assumption of steady-state conditions, also show the influence of the biogeochemical processes of phytoplankton uptake and sinking fluxes of particle associated POPs. In upwelling regions where the dissolved phase of the mixed layer is depleted in POPs, enhanced sinking fluxes are observed, due to higher fluxes of organic matter driven by the higher primary productivity. The increase in sinking and air–water fluxes is observed for all the PCBs, PCDDs, and PCDFs studied but is more apparent for the more hydrophobic compounds. It clearly shows that biogeochemical processes occurring in the water column affect depositional processes, particularly diffusive air–water exchange of POPs.

The latitudinal profiles of air–water and sinking fluxes show some trends that complicate the “global distillation” paradigm. For example, the depositional fluxes of PCB 180 (Figure 4) and of other hydrophobic chemicals do not increase at high latitude in comparison to the tropical and subtropical areas. Conversely, an increase of air–water fluxes at mid-high latitudes is observed for chemicals with lower hydrophobicity (Figure 3C). High latitudes are characterized by both low temperatures and high primary productivity. To differentiate the contribution of each variable to the transport of POPs from the atmosphere to the deep ocean, we need to return to the mass transfer coefficients.

**Processes Driving the Oceanic Fate of POPs at the Global Scale.** A single equation may be derived for the overall transport of POPs from the atmospheric gas-phase to deep waters using eqs 1, 7, 9, and 12

\[
F_{ADW} = k_{ADW} C_{A} W^{-1}
\]

where \( F_{ADW} \) (ng m\(^{-2} \cdot \text{d}^{-1} \)) is the flux of POP between the atmosphere and deep waters, and \( k_{ADW} \) (m d\(^{-1} \)) is the air-deep water mass transfer coefficient given by (see Annex I in the Supporting Information)

\[
k_{ADW} = \frac{k_{WP} k_{Sink} + k_{Sink} + k_{Sink} k_{WP} + k_{Sink}}{k_{Sink} + k_{Sink}}
\]

Under steady-state conditions this flux depends on the gas-phase concentrations of POPs, the dimensionless Henry’s law constant and on the overall air–deep water mass transfer coefficient. Temperature influences \( H^* \) and, as suggested by the global distillation hypothesis, will tend to enhance fluxes at high latitudes. However, \( F_{ADW} \) also depends linearly on \( k_{ADW} \). From eq 14, it follows that the process having the lower mass transfer coefficient will be the limiting step in the overall air–deep water transport. As discussed above, adsorption to
plankton is a very fast process and thus it is not the limiting step. Similarly, \( k_{WP} \) is also almost always higher than \( k_{AW} \) and \( k_{Sink} \) (Figure 2) and thus it will rarely be the limiting step in the air-deep water exchange. Therefore, either air–water exchange or sinking of particulate matter will be the rate-limiting process constraining the overall flux. Figure 5 shows a comparison of the Atlantic Ocean latitude-averaged values of \( k_{AW} \) and \( k_{Sink} \) for PCBs 52 and 180. For chemicals with low to moderate hydrophobicities (ca. log \( k_{OW} \) < 6), such as PCB52, air–water exchange is faster than sinking of particle associated POPs. Therefore, the air–water exchange will keep surface water concentrations in conditions close to equilibrium with the atmospheric gas-phase, except in areas with very high primary productivity (ca. Bp > 1 mg L\(^{-1}\)). The occurrence of equilibrium conditions can be assessed by means of the ratio of gas-phase (\( f_A \)) and dissolved phase (\( f_W \)) POP fugacities given by (46)

\[
\begin{align*}
  f_A &= C_A \cdot R \cdot T \quad (15) \\
  f_W &= C_W \cdot H \quad (16)
\end{align*}
\]

The fugacity ratios \( f_A / f_W \) for PCB 52 and PCB 180 are shown in Figure 5. The fugacity ratios can be measured directly from eqs 15 and 16 or from \( k_{AW} \) and \( k_{ADW} \) by (see Annex II)
Therefore, the analysis of the fugacity ratios is independent of the gas-phase database considered. This is important since uncertainty associated to estimated $k_{AW}$ and $k_{ADW}$ from remote sensing measurements is lower than that associated with the measurement of PCB gas-phase concentrations over the ocean.

The latitude-averaged fugacity ratios of PCB 52 are close to 1 over nearly all latitudes, with the exception of regions with very high primary productivity such as upwelling areas. For chemicals with low hydrophobicities, such as PCB 52, the sinking flux is the limiting step and thus $k_{Sink}$ contributes to a greater extent than $k_{AW}$ and $k_{WP}$ to $k_{ADW}$ (see eq 14). Therefore, the increase of fluxes at mid-high latitudes are due in part to the higher values of $k_{Sink}$, and thus of $k_{ADW}$, driven by the high fluxes of organic matter and associated POPs in these regions. Recently, conditions close to equilibrium have been reported for HCHs in the Atlantic Ocean (47). Since HCHs also have low hydrophobicities, the scenario for this compound would be similar to that of low chlorinated PCBs.

The scenario differs for POPs with moderate to high hydrophobicities ($\log K_{OW} > 6$), such as PCB 180, for which...

\[
\frac{f_A}{f_W} = \frac{1}{1 - \frac{k_{ADW}}{k_{AW}}} \tag{17}
\]
Sink values are much higher. In addition, these chemicals have lower diffusivities and $H'$ values than lower chlorinated PCBs that lead to lower $k_{AW}$ values. The comparison of $k_{AW}$ and $k_{Sink}$ values (Figure 5) shows that air—water exchange is faster in low latitude areas, while sinking fluxes are faster in mid to high latitudes areas. In these oceanic regions, air—water exchange is not fast enough to compensate the depletion of POPs in the surface mixed layer, due to vertical fluxes of particle-associated POPs. The analysis of fugacity ratios (Figure 5) show strong disequilibria at mid-high latitudes, due to depletion of water column concentrations. Figure 4 shows that air—water and sinking fluxes at high latitudes are moderately high, given that the corresponding gas-phase concentrations are very low. This is due to the high gradients that hydrophobic compounds have between air and water concentrations and thus enhancing air—water fluxes. The behavior of the most chlorinated PCBs is similar to that shown for other very hydrophobic POPs. For example, Figure 6 shows the fugacity ratios for the tetra- and hexa-chlorinated dibenzo-dioxins ($Cl_4DD$ and $Cl_6DD$). In the case of PCDDs, most show a depletion of dissolved phase concentrations at high latitudes driven by the high settling fluxes in the areas with high primary productivity. Therefore, in these areas the air—water depositional fluxes of PCDD/Fs will be enhanced as the result of the biological pump. The comparison of the fugacity ratios for $Cl_4DD$ and $Cl_6DD$ also show that the greater the hydrophobicity of the chemical, the greater is the fugacity gradient in the high primary productivity areas.

The relative importance of air—water exchange and vertical fluxes as controlling processes of the global dynamics of POPs are, to a certain extent, independent of the magnitude of gas-phase concentrations of POPs. Indeed, the rate-limiting process depends on the values of the mass transfer coefficients and in fact the fugacity ratio can also be derived from these mass transfer coefficients if steady state is assumed (Annex II). Therefore, the conclusions reached above on the importance of the biological pump for the sequestration and...

**FIGURE 5.** Comparison of $k_{AW}$ and $k_{Sink}$ for (A) PCB 52, (B) PCB 180, and (C) fugacity ratios for PCB 52 and 180.

**FIGURE 6.** Comparison of $k_{AW}$ and $k_{Sink}$ for (A) tetra-chlorinated dibenzo dioxins ($Cl_4DD$), (B) hexa chlorinated dibenzo dioxins ($Cl_6DD$), and (C) fugacity ratios for $Cl_4DD$ and $Cl_6DD$. 
global dynamics of POPs are independent of the assumptions done in the present study.

In summary, biogeochemical processes and specifically, phytoplankton uptake and the subsequent sinking to deep waters play a major role determining air–water fluxes and the ultimate sink of POPs. For chemicals with low hydrophobicity, this is due to higher values of $K_{OW}$, while for very hydrophobic chemicals, enhanced fluxes are found at mid-high latitudes due to depletion of water column concentrations and thus increased concentration gradients. The present work suggests that the influence of biogeochemical processes controlling water column concentrations and vertical fluxes of particle associated POPs may be as important as temperature as factors driving the global fate, transport, and sinks of POPs.

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Supporting Information Available

The procedure to obtain eq 14 (Annex I) and the arithmetics leading to eq 17 (Annex II). This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited


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