Results and discussion

Biogeochemistry is a Major Driver of the Atmospheric Residence Times and "Grasshopping" of Persistent Organic Pollutants over the Oceans

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Abstract

Knowledge of the processes driving the atmospheric residence times and the grasshopper potential are key for understanding regional and global fate and distribution of Persistent Organic Pollutants. Here, these processes have been investigated for polychlorinated biphenyls by means of a pioneering modeling approach that combines retrieved satellite environmental parameters and POP fate and transport models, so that their spatial and seasonal variability are accounted. Residence times result highly variable and dependent on physicochemical properties of the compound, especially on its degree of hydrophobicity, and as well on spatial distribution of waters column removal processes of POPs. The number of hops that a chemical undergoes when being transported in the atmosphere over the oceans also presents an important patchiness related to settling fluxes. Therefore, it is found that water column biogeochemistry controls the atmospheric residence times and number of hops in mid-high latitudes and in upwelling areas. In these areas temperature exerts a less determinant role, while still being important, in the control of the atmospheric deposition due to OH attack in subtropical regions. The settling of particle bound compounds becomes determinant for highly hydrophobic compounds and its influence is minor for less hydrophobic ones, where degradation by radical OH is the dominating sink due in part to close to equilibrium conditions between the surface ocean and lower atmosphere.

1. Introduction

Persistent Organic Pollutants (POPs) are toxic and bioaccumulative compounds that have been detected in all environmental compartments, even in remote pristine regions where they have never been produced or used (1,2). Two essential properties defining these contaminants are their persistence and
their potential for migrating thousands of km, i.e. long-range atmospheric transport (LRAT). This potential for LRAT is important since atmospheric transport and subsequent deposition is the major route of introduction of POPs to the oceans, and thus to the marine food webs (4,5). It has been suggested that when long-lived and semi-volatile substances travel through the atmosphere, they tend to move in stages. This is known as the grasshopper effect, a repeated (and often seasonal and/or diurnal) process of volatilization and deposition. Essentially they can reach the colder regions of the Arctic and other pristine environments. Temperature plays a key role in driving the magnitude of air-surface partitioning (6,7), and thus exerts an influence on the ratio of gas to dissolved phase concentrations. One step forward, it is suggesting that temperature also influences the fluxes between air and water (6-8), something that has not been proved experimentally and dependent on the water column inventories. In fact, recently it has been shown that other variables than temperature such as biomass distribution, depth of the mixing layer, etc., also play a key role in controlling the reservoir capacity of oceans, soils and vegetation for POPs (9-11). Concerning the fluxes, biogeochemistry do play a critical role in controlling the dissolved phase concentration, and thus the air water gradient of POP concentrations, key in determining the direction and magnitude of deposition fluxes (12). The atmospheric residence times and transport of POPs over the ocean will depend on these atmospheric deposition fluxes.

Models do provide the appropriate approach to quantify the overall persistence and potential for LRAT, since experimental approaches can in most cases only provide insight into the persistence in a certain environmental compartment, but not in the chemoherm due to experimental and operations limitations. Indeed, persistence and LRAT of POPs are function of the mode of entry in the environment and a complex interplay of processes affecting their fate and transport (7,12,14). Among these processes and in the atmosphere over the open-oceans, it should be stressed the role of removal fluxes such as dry deposition of aerosol-bound compounds, scavenging of contaminants by rain, also termed by wet deposition, diffusive absorption to the ocean and degradation by the OH radical. Input fluxes to the atmosphere are mainly volatilization of POPs from the water masses (15).

A large number of models have quantified persistence and LRAT under a number of different measures of residence time and transport distance. In particular, the \textit{residence time} is an indicator of persistence and gives insights of the average life expectancy of a pollutant in an environmental compartment. It is generally calculated at steady-state and estimated as the mass divided by the output rate. However, under unsteady state or dynamic conditions, it is sometimes referred as \textit{characteristic time}. On the other hand, \textit{Half-Life} is defined as the time span within which the chemical concentration decays by 50% of the initial concentration value. In other fields dealing with chemicals other than POPs, Junge (16) found an empirical relationship between residence time and standard spatial variation.
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In concentration, an idea that has been applied recently (17) to a multiazelia model and for residence times of POPs in the atmosphere. Deviations from the Lange relationship when comparing to field data has been found for POPs that are associated to an important transport in water, and in substances with a strong tendency for re-volatilisation. The importance of re-volatilisation is key to understand the cycling and transport of POPs in the atmosphere. LRAT can also be calculated and expressed in a number of ways. It can be regarded as the average distance a chemical moves half-distance as suggested by Van Pol et al. (18), as the distance travelled at which half of the original chemical mass remains, and characteristic travel distance at which remains the 57% (19). Another approach to compute LRAT is considering the distance within most of the chemical is retained when the chemical is distributed as steady-state within the environment. This latter approach has been used with eulerian models, computing for example a spatial range as the distance within which the 95% of the substance is retained when the chemical is distributed (20).

Since a direct validation of these measures is not possible, conclusive results of model comparison studies are difficult and the validity of the values depends on the configuration and context within the model is used (21,22). However, important limitations are present in most models such as the use of constant mass transfer coefficients, i.e. constant dry deposition velocities, washouts, etc., or the lack of a spatial variability in the processes affecting POPs. It is especially evident in box models with nested or circular configurations (20,23). Furthermore, the interplay with the biogeochemical processes occurring in the ocean has been overlooked, even though previous studies have demonstrated that they may affect significantly the air-water transfer of POPs and thus their persistence and LRAT (9,12,24).

In particular settling of particle bound to the deep oceans plays a major role in areas with high primary productivity and for high hydrophobic compounds. Indeed, the biological pump acts deactivating the system from equilibrium conditions, otherwise air-water exchange that keeps surface water concentrations in conditions close to equilibrium with the atmospheric gas-phase concentrations (12). Temperature alone cannot account for this equilibrium-dequilibrium conditions in different oceanic regions. Sometimes, there has been confusion when assuming that lower temperatures also imply higher dry deposition rates, as suggested for the Arctic. This will not be valid, since and water are close to equilibrium, since a higher gross deposition rate could be compensated by a higher volatilization rate.

Therefore, in order to understand net deposition fluxes and thus atmospheric residence times, it is important to assess the processes removing POPs from the atmosphere and replenishing them. Therefore, the objectives of this work are: i) to compute spatially and temporally resolved atmospheric residence times over the global oceans, ii) analyze the influence of biogeochemical related processes of POPs to the atmospheric residence times, iii) investigate whether or not these are biogeochemical controls on “grasshopping”, and iv) determine the dominant process regulating the atmospheric...
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residence times. These issues are studied by combining fate and transport models with satellite retrieved data that provide global coverage of the oceans, which were developed previously and proven to agree within a factor of 2 in most cases with measurements (25,26).

2. Methods

2.1 Parameterization of the residence time

The residence time $t$ [s] is defined here as the time that the concentration of a contaminant decreases until it reaches a concentration $1/e$ of the initial value. Both removal and input fluxes are accounted. Therefore:

$$
\frac{\text{Inventory}}{\text{Input Fluxes} - \text{Output Fluxes}} = t \frac{1}{V_c} \left( \frac{V_{C_0}}{V_{C_{0,1}}} \right)
$$

The previous equation, when applied over remote ocean atmospheres becomes:

$$
t = \frac{V_{C_0}}{V_{C_{0,1}}} \frac{\tau_{w,\text{deg}} + \tau_{w,\text{vol}} + \tau_{w,\text{dep}} + \tau_{w,\text{vol}} - \tau_{w,\text{vol}}}{\tau_{w,\text{vol}} + \tau_{w,\text{vol}} + \tau_{w,\text{vol}} - \tau_{w,\text{vol}}}
$$

where $\tau_{w,\text{abs}}$ [s] is the dry deposition decay rate, $\tau_{w,\text{deg}}$ [s] the gaseous absorption decay rate, $\tau_{w,\text{vol}}$ [s] the wet deposition decay rate, $\tau_{w,\text{deg}}$ [s] the degradation decay rate and $\tau_{w,\text{vol}}$ [s] the volatilization input rate. It is easily deduced from above that the total decay rate is given by

$$
\frac{1}{\tau_{w,\text{vol}}} = \frac{1}{\tau_{w,\text{vol}} + \tau_{w,\text{vol}} + \tau_{w,\text{vol}} - \tau_{w,\text{vol}}}
$$

By means of simplification, it has been assumed that the pollutant is homogeneously distributed in the atmosphere. Boundary layer (ABL) [m] of height $h$ [m] and volume $V$ [m$^3$] and with an atmospheric inventory dominated by gas phase compounds and homogeneously distributed, $C_0$ [ng m$^{-3}$]. Furthermore, inputs and losses with the free troposphere have been neglected, which is a common assumption in the open ocean atmospheres.

Each decay rate has been derived from the corresponding flux parameterizations presented in Immel et al. (25,26) and Dachs et al. (12). They refer to fluxes computed over the global oceans, as in the present exercise, and also derived from meteorological satellite input data, as explained in (25,26). Therefore, it can be deduced that:
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\[ \tau_{W_{\text{air}}} = \left( \frac{k_{W_{\text{air}}}}{H} \right)^{1-\phi} \left( 1 - \frac{k_{W_{\text{air}}}}{H} \right)^{\phi} \]

\[ r_{W_{\text{air}}} = \left( \frac{k_{W_{\text{air}}} - k_{W_{\text{air}}}}{H} \right)^{1-\phi} \left( 1 - \frac{k_{W_{\text{air}}} - k_{W_{\text{air}}}}{H} \right)^{\phi} \]

\[ \tau_{d} = \frac{\phi \cdot D}{(1 - \phi) \cdot h} \]

\[ \eta_{d} = \frac{(W_{d} + W_{p}) \cdot D}{(1 - \phi) \cdot h} \]

where \( k_{W_{\text{air}}} \) [m s\(^{-1}\)] is the air-water mass transfer coefficient, and \( k_{W_{\text{air}}} \) [m s\(^{-1}\)] is the air deep water mass transfer coefficient. The latter has been determined as described in Dachs et al. (12) and characterizes the overall transport of POPs from the atmospheric gas phase to deep waters, i.e. relays the air-water exchange to the phytoplankton uptake and particle sinking. When the mixing subscripts is added, it is accounted the enhancement of \( k_{W_{\text{air}}} \) due to the turbulence generated by rain (27), as discussed in Junaro et al. (26). \( H \) accounts for the dimensionless Henry's law constant, itself derived from Brunner et al. reference values (28), and \( \phi \) is the fraction of contaminants bound to aerosols in the atmosphere, dependent on the temperature, the organic matter content and amount of total atmospheric suspended matter \( (\text{TSP} \text{[mg m}^{-3}] \) among other factors: \( \phi = K_{w} \text{TSP}^{1/5} \text{[1} + K_{w} \text{TSP]} \). In this exercise \( K_{w} \) was modeled as absorption into the organic matter (29) and adsorption onto soot aerosol which may be relevant for the more co-planar compounds (30). \( V_{d} \) [m s\(^{-1}\)] is the dry deposition velocity, dependent on aerosol size and on the wind speed (31) and modeled over the global oceans from remote sensing derived parameters as shown in Junaro et al. (35). Finally \( W_{d} \) and \( W_{p} \) are the gaseous and particle washouts, the first assumed as the addition of the absorption and adsorption onto the raindrop (26,32), the second assumed to be constant and equal to \( 2 \times 10^{4} \text{[m s}^{-1}] \).

On the other hand, the POP degradation in the atmosphere is assumed to be dominated by the reaction with hydroxyl radicals and considered to be occurring only in the gas-phase. The corresponding decay rate is formulated as follows:

\[ \tau_{d} = k_{d}[OH] \]

where \( [OH] \) [mole/L cm\(^{-3}\)] is the concentration of OH radical and \( k_{d} \) [cm\(^{3}\) mole\(^{-1}\) s\(^{-1}\)] is the degradation rate constant for air \( C_{OH} \) vary substantially in the atmosphere and are strongly correlated to the
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The intensity of sunlight, with night time concentrations orders of magnitude lower than those observed during the day. Its distribution at a global scale has been computed using following formula: where the hydroxyl concentration is directly related to temperature; \( C_{OH} = 0.5 \times (T - 273.15) \times 10^{-4} \) (7). On the other hand, temperature dependence of rate constant of the gas phase reaction with \( \text{O}_3 \) radical is taken in the form of Arrhenius equation, so that higher degradation rates occur in warmer regions. Finally, the reference \( k_{OH} \) values at 298 K are determined in Brotaker and Hines (34).

It is of significant interest to evaluate the number of "hops" that the chemical undergoes at the global scale over the ocean. Each hop is assessed as a volatilization followed by a subsequent deposition, thus if a substance has a large number of hops it may travel further than a substance that has a few number of hops, thus becoming an indicator of POP recycling in the stratosphere. It has been evaluated in this exercise as the residence time as computed in eq. 1, divided by the time a certain molecule of contaminant flushes out of the atmospheric compartment. This latter term doesn't account for the reverbalization of POPs from water masses and is expressed in fact by the inventory of contaminants divided by the output rate

\[
\text{hop} = \frac{\text{time to decrease}}{\text{output rate}}
\]

Indeed, the denominator in equation 8 is the residence time of a certain molecule in the atmosphere, which is always lower than the time required to decrease the concentrations to 1/\( e \) of the initial values. This is due to the fact that volatilization replenishes the atmosphere with POPs. Therefore, equation 8 is an indicator of the average number of times that molecules should volatilize deposit (hops) during the average residence time of the chemical (time to decrease the atmospheric concentration).

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3.1 Residence times of POPs in the ocean atmospheres

Residence time at each point of the global ocean were computed using the equations 1 / 7 and satellite derived meteorological input. Resulting maps (Figs. 1) of resolution of 1°x1° provide novel insights of the spatial and temporal variability of the residence time of POPs.
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It is easily appreciated the spatial and seasonal variability of residence times. This variability results from the variability of environmental conditions such as wind speed, sea surface temperature, phytoplankton biomass, precipitation rate, OH concentrations, etc. and is also highly dependent on the physicochemical properties of the compound. Indeed compounds with low to moderate hydrophobicities present residence times that vary with lower steep gradients and increasing residence times towards mid-high latitudes (see Figure 1A – 1B). Their distribution supports an equilibrium distribution of gas-phase concentration with small variation in concentrations during atmospheric transport due to their long residence times. Lower residence times are in the intertropical regions due to enhanced degradation by OH radical attack. Different trends appear for the more hydrophobic congeners such as PCB 180 (Figure 1C – 1D). Their propensity to attach to the particle and rain drops induces higher deposition rates. Furthermore, degradation rates by OH radical are low for these congeners. Finally, their high hydrophobicity mean that they have a high tendency to sink to settling.
particles and thus allowing the biological pump to be an efficient removing mechanism of POPs from the atmosphere to deep waters. Especially important is the influence of high productivity areas, with higher settling fluxes and to a higher tendency to sink to deep waters. It has been stressed previously (1,2) the role of the sinking fluxes driving higher net gaseous diffusive absorption fluxes and thus lowering atmospheric residence times. This is evident (see Figure 1) in upwelling areas (off Sahara, off Namibia, ...) and high latitude oceanic regions. Indeed it is driven by the distribution of phytoplankton productivity, highly patchy (3,5). Therefore it is important to study the spatial and seasonal variability of the biological pump. Its strength can be described by means of $k_{EANP}/W$, which is the driving gas-phase mass transfer coefficient of the air deep water flux (1,2) and is represented in Figure 2:

![Diagram](image_url)

Figure 2: Strength of the “biological pump”, quantified by $k_{EANP}/W$. Refer to PCB 28 (Figure 2A and 2B) and PCB 180 (Figure 2C and 2D) in January and July.
Figure 2 shows the strength of the biological pump in mid-high latitudes and for highly hydrophobic POPs. Furthermore, comparing Figure 2 with Figure 1, the role of settling of particle-bound compounds is clear and explains the differences of the residence times depending on hydrophobicity. Figure 3A and 3B show that residence times of the less chlorinated PCBs do not decrease at higher latitudes, this may seem surprising at first sight, since at lower temperatures, gross absorptive, dry and wet fluxes are higher, but for these congeners settling of particle-associated flux is not fast enough to drive air and water out of equilibrium as demonstrated elsewhere (see figure 5 of Dachs et al. 2002 and discussion therein). Therefore, the gross volatilization is of similar magnitude to the gross deposition resulting in long atmospheric residence times. This shows that intuitive patterns and very much used working hypothesis that assume that at lower temperatures deposition is higher are wrong. In water column biogeochemistry what controls the atmospheric residence times at high latitudes and in upwelling areas. Nevertheless, temperature does play a role as a driver of atmospheric degradation due to OH attack in intertropical regions. Low temperatures also play a certain role in enhancing the fraction of water column POPs associated to particles, but the modification of POP settling fluxes due to temperature is much lower than due to different trophic status, which result in fluxes of organic matter that can vary by orders of magnitude.

3.2 Drivers of POP atmospheric residence times
An analysis of the decay rates, previously described in eq. 3-7, provides a simple procedure to determine the dominant process affecting the residence times of POPs. We have distinguished between decay rates due to deposition and air water exchange, i.e. fluxes of transfer of POPs between air and water \( r_{dep} \) and \( r_{air_water} \), and the decay rates due to degradation, i.e. \( r_{deg} \). Then, the process having the major decay rate is the dominant process controlling the atmospheric residence time. The representation of the ratio \( r_{dep}/r_{air_water} \) shows a dominant degradation flux for the less hydrophobic compounds (Figure 3A). A different situation occurs for highly hydrophobic congeners. They are mostly controlled by atmospheric deposition, or \( r_{dep} \) (Figure 3B).
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Figure 3: Global distribution of the ratio $x_{air}/x_{water}$ for PCB 28 (Figure 4A) and PCB 180 (Figure 4B) in July. When it is major than 1, degradation fluxes dominate, otherwise fluxes that transfer POPs between air and water dominate.

Figures presented before represent two extreme situations. The dominance of $x_{air}$ in most of the tropical ocean regions may be a common situation only for PCBs with low hydrophobicities ($\log K_{ow}$s). For other PCBs $x_{water}$ plays a major role, since degradation rates are low. In the magnitude and direction of the different “transfer fluxes”, air-water exchange plays a major role for contaminants found mainly in the gas-phase such as PCBs. It acts leading to keep dissolved concentrations in surface waters close to equilibrium with the atmospheric gas-phase concentrations. However, its magnitude and direction is altered and determined by sinking fluxes. Indeed what controls the residence times is basically sinking process, a non-fugacity based flux and irreversible since once POPs are transfers to deep waters they can not recycle back in the atmosphere and undergo further biodegradation.

3.4 Transport potential due to the “grasshopper effect”

The number of “hop” that compounds undergo when travelling is depicted in Figure 4. Maximum are found in mid-high latitudes for lower hydrophobic PCB compounds and in tropical areas for the more hydrophobic ones. Such difference is clearly influenced by the major influence of the degradation fluxes for the low chlorinated, acting principally in tropical areas. Also the major tendency of the more hydrophobic PCBs to sink and to be scavenged by rains (in the particle phase) is
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determinants to diminish the number of hops in mid-high latitudes, upwelling areas, and regions with high precipitation rates.

Such observations cannot be accounted if residence times and grasshopping potential are supposed to be a function primarily of temperature. In Figure 4 it is observed some patchiness which is not explained by the uniform temperature gradient. Indeed, as commented above, temperature does play a role increasing the gross deposition fluxes, and if the average time that a certain molecule remain in the atmosphere is plotted (see Figure A1 in the Supporting Information), as given by the denominator of equation 8, then it is seen that these times decrease following remarkably the spatial variability of temperature. However, air-water concentrations of POPs with low to mild hydrophobicities are close to equilibrium (12,36), and thus solubilization fluxes replenish the atmosphere imparting a significant diurnal to atmospheric concentrations.
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These trends are evidently related to stiffness as defined elsewhere as the fraction of deposited POP that does not volatilize (37), and thus related to the net atmosphere to surface flux. The major removal or loss flux from the surface ocean is settling to deep waters, therefore, stiffness is directly proportional to the air-sea fluxes, and thus to k_{settling} as depicted in Figure 2. Therefore, where settling fluxes are higher, the stiffness will be higher, and the grasshopping potential lower.

From all that has been discussed above, it is possible to state that the global fractionation processes may occur, but are a complex interplay of many processes and water column biogeochemistry plays a dominant role among them. Indeed, here we prove that atmospheric occurrence of POPs is also a function of biogeochemical parameters, such as phytoplankton biomass, and variability in deposition fluxes due to other factors than temperature (aerosol concentrations, precipitation rates, etc). Other recent reports have implicitly or explicitly pointed to the potential role of settling fluxes in residence times (12,32), but its effect was not compared to that of temperature, and spatial variability was not assessed as done here. As a result, the less chlorinated PCBs have a tendency to be degraded in situ in tropical areas, but at latitudes higher than 30°N or 30°S they have long atmospheric residence times. Less volatile compounds, instead, may hop in tropical areas, but tend to be irreversibly deposited in mid-high latitudes.

Furthermore, this work offers an opportunity to review the influence of temperature on POP cycling, which is important to explain the air to water ratio of concentrations, but not sufficient for explaining the global inventories of POPs (9,11), and as shown here, is not the primary driver of the atmospheric residence time and grasshopping of POPs over many oceanic regions.

Acknowledgements

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Supporting information available

The Figure A1, showing the average time that a certain molecule remains in the atmosphere concentration is found in the Supporting Information.
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Biogeochemistry is a Major Driver of the Atmospheric Residence Times and “Grasstopping” of Persistent Organic Pollutants over the Oceans

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SUPPLEMENTARY MATERIAL

Figure A1: Average time that a certain molecule remains in the atmosphere for PCB 28 (A,B) and PCB 180 (C,D) in January and July.
3.2.3.5 **Scientific contribution:**

*Oceanic deep water formation as a sink of persistent organic pollutants*

Lohmann, R., Jurado, E., Pilson, M. E. Q., Dachs, J.

Lohmann, R.: interpretation and writing
Jurado, E.: modelling support, interpretation
Pilson, M. E. Q.: physical interpretation of deep-water formation
Dachs, J.: interpretation
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Oceanic deep water formation as a sink of persistent organic pollutants

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The formation of deep oceanic waters occurs as part of the global thermohaline circulation due to differences in salinity and temperature, and moves surface waters rich in persistent organic pollutants (POPs), directly to the deep ocean. For the four main deep water formation regions, annual fluxes of polybrominated biphenyl (PBB) congeners were calculated based on their surface water concentrations and deep water formation rates. PBB fluxes were highest in the Norwegian Sea (ca. 470 kg pyr yr⁻¹) and the Labrador, Ross, and Weddell Seas (ca. 149 – 168 kg pyr yr⁻¹). These regions were identified as important in the global thermohaline circulation due to differences in salinity and temperature, and moves surface waters rich in POPs, directly to the deep ocean. The formation of deep oceanic waters is especially important in the North Atlantic (Norwegian and Labrador Seas) and the southern oceans (Weddell and Ross Seas). The importance of ventilation as a means of removing POPs from the surface ocean is discussed with respect to their global fate.

1. Introduction

1.1 Polybrominated biphenyls (PBBs) are a group of pollutants urged by the Stockholm treaty as Persistent Organic Pollutants' (POPs) because of their persistence, adverse effects, potential for long-range transport and their ability to bioaccumulate in the food chain. Recent work has investigated the global flux of POPs, temporary reservoirs include global soils and vegetation [Majeski et al., 2002; Latthe et al., 2003], while short residence [Johansson et al., 2003], the deep ocean [Dachs et al., 2002] and, potentially the atmosphere [Azevedo and Colaresi, 2002] represent final sinks. In previous work we have presented a framework to estimate the oceanic sink of POPs associated with settling particles, based on atmospheric concentrations and a series of partitioning steps through dry and wet deposition, phytoplankton uptake and removal from the surface mixed layer by the organic carbon settling flux [Dachs et al., 1999, 2002]. However, no estimate has been made of the importance of formation of oceanic deep water on the removal of POPs from the surface ocean, which is an important global reservoir of POPs [Dachs et al., 2004a]. The objective of this work is to estimate the importance of this overlooked contribution to the marine sink of organic pollutants. Subduction or formation of deep oceanic waters occurs as part of the global thermohaline circulation due to differences in salinity and temperature, by convecting directly oceanic waters, including PCBs, to the deep ocean [e.g., Broecker, 1974]. The formation of deep oceanic waters is especially important in the North Atlantic (Norwegian and Labrador Seas) and the southern oceans (Weddell and Ross Seas). The importance of ventilation as a means of removing POPs from the surface ocean is discussed with respect to their global fate.

2. Materials and Methods

2.1 Regions With Relevant Formation of Deep Oceanic Water

2.1.1 The following regions were considered in the northern North Atlantic, the Norwegian Sea and Labrador Sea; in the Southern Ocean, the Weddell and Ross Seas. These regions are relevant to the main deep water formation sites of the deep ocean [Hansen et al., 2002]. As a means of simplification, each region was assumed to be a nutrient rich basin with a characteristic deep water formation rate. The boundary conditions and water transport rates were:

- (i) Norwegian Sea (60°N–30°N, 0°–58°E); (ii) Labrador Sea (55°N–5°N, 55°W–20°W); (iii) Weddell Sea (60°S–65°S, 40°W–50°W); (iv) Ross Sea (60°S–80°S, 110°E–150°W); (v) Norwegian Sea (10°S–10°N, 5°E–20°W).

2.2. Estimation of PCB Oceanic Deep Water Formation and Sinking Fluxes

2.2.1 The subduction flux of a given region and compound (PBC, kg m⁻² s⁻¹) was parameterized in the position of the water chemical composition concentration (defined for particulate phase) (CWP, ppb L⁻¹) and the rate of deep water formation of the chosen area (f, s⁻¹) divided by the area of interest (A, m²), where 1.55 10⁻⁶ s m⁻¹ L⁻¹ m⁻³ is a conversion factor.

EPCB = CWP × f / A

2.2.2 The sinking flux (PBC_sinking, kg m⁻² s⁻¹), which has been identified as a key process in understanding the global dynamics and oceanic sinks of POPs [Dachs et al., 1999, 2002], was defined as the settling flux of particle associated concentrations. The sinking flux was estimated from the PCB concentration in the particulate organic matter phase.
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Table 1. Different Oceanic Deep Water Formation Regions Considered (1 × 10^6 m^3 s^-1) and Respectively Measured on Derived POPs Water Concentrations (ng kg^-1)

<table>
<thead>
<tr>
<th>Region</th>
<th>POPs</th>
<th>POPs</th>
<th>POPs</th>
<th>POPs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Norwegian Sea</td>
<td>10</td>
<td>97</td>
<td>87</td>
<td>97</td>
</tr>
<tr>
<td>Baltic Sea</td>
<td>40</td>
<td>36</td>
<td>23</td>
<td>35</td>
</tr>
<tr>
<td>Strait</td>
<td>95</td>
<td>17</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Total</td>
<td>1,100</td>
<td>790</td>
<td>2,000</td>
<td>720</td>
</tr>
</tbody>
</table>

(\(C_{\text{POP}}\) in ng kg^-1) and the vertical flux of organic matter (\(F_{\text{org}}\), kg m^-2 y^-1)

\[ F_{\text{org}} = \frac{C_{\text{org}}}{C_{\text{POP}}} \]

(1) These fluxes were estimated as detailed elsewhere (Duchêne et al., 2002; Jourde et al., 2003a, 2003b). Briefly, phytoplankton biomass was assumed to account for the majority of particulate organic carbon, and was estimated from chlorophyll a concentrations (\(C_{\text{chl}}\)) using Jourde et al., 2003a. \(C_{\text{chl}}\) was estimated from dissolved or water or oceanic areas using the binoculation factor as described elsewhere (Duchêne et al., 2002; Jourde et al., 2003b). The netting time of organic carbon (\(B_{\text{org}}\)) was estimated from \(C_{\text{chl}}\) as given by Rassoul and Parce (1984).

(2) Both POP and sinking fluxes were estimated from POP water concentrations (Table 1). When measurements of POPs were not available, water concentrations were estimated from the reported gas-water concentrations (Table 1) using a 1-dimensional model that considered air-water exchange, phytoplankton uptake and sinking at long term steady state (Duchêne et al., 2003a; Jourde et al., 2003b).

2.2. Data Sources of Oceanic Occurrence of POPs and Geographical Variables

(4) This work was based on surface water concentrations - dissolved plus particulate - of seven widely studied POP congeners (PCB 26, 52, 101, 118, 138, 153, 180). They were measured during sampling transects or at stations in the regions of interest defined above (Jourde and Gustafsson, 2004; Stabell et al., 1993). As discussed by Biering et al. (2001), these recent measurements are likely to be more POP water concentrations, as they were obtained by either in situ pumps (Stabell et al., 1993) or on the FS Polarstern, which was considered a “clean” ship (Stabell et al., unpublished data, 2000; R. Lohmann et al., unpublished data, 2004).

(5) However, due to the scarcity of POPs concentrations in the open ocean, particularly in the Northern Hemisphere, when evaluating the Weddell and Ross Seas, POP water concentrations were derived from gas-water concentrations (Jourde et al., 2003a) and POP concentrations reported by Montani et al. (2001) for King George Island resulted in much too elevated water concentrations, despite of a localized contamination problem. Table 1 shows the data sources of POP water concentrations for the oceanic regions assessed. Table 2 shows the POPs concentration times in the different regions. Briefly, in surface waters, patterns of relative abundance of the different POP congeners were similar; in deeper waters, a depletion of the lower containing congeners became apparent.

(6) Meteorological data was retrieved from remote sensing measurements as reported elsewhere (Jourde et al., 2002). Near Northern Temperatures (KWT, K) were obtained from the Atog Track Scanning Radiometer (ATSR) (http://www.atos.cea.fr/atis/atiss.html) and the MODIS satellite (http://modis.gsfc.nasa.gov/). These measurements represent average values from three consecutive years (1999–2001) of monthly mean temperatures, with a 1° × 1° resolution.

3. Results and Discussion

3.1. Oceanic Deep Water Formation Rates of POPs

(7) The mean POP fluxes associated with the formation of deep oceanic water varied between the four regions (Figure 1). POP fluxes were highest in the Norwegian Sea (ca. 350 ng m^-2 y^-1), and least important in the Labrador, Weddell and Ross Sea (ca. 90, 70 and 150 ng m^-2 y^-1, respectively). This is in part due to lower atmospheric and oceanic water concentrations in the southern hemisphere. Indeed, the majority of POPs have been produced and used in the Northern hemisphere, mainly in Western Europe and...
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North America (Brinkhaus et al., 2002a, 2002b). Detailed PCB concentrations in atmosphere and surface waters are therefore expected in the northern hemisphere. The ratio of the sum of deep water samples of the Norwegian, Ross and Weddell Seas are all estimated to be around 10 - 15 Sv each. This flux estimate differs mainly because of different surface water concentrations, especially for the lower chlorinated PCBs.

[165] Indeed, the trends for the individual PCBs considered here show the higher Os 26, 52 and 101 to be most important in the Labrador and Norwegian Seas, whereas PCBs 138 and 153 (and 78) are equally important congeners in the southern subduction regions (Table 1 and Figure 1). This shift from the lighter congeners being more important in the Northern hemisphere toward the heavier congeners in the Southern hemisphere could reflect differences in long-range transport and atmospheric deposition (Kroenke and Gage, 2005). However, as the PCBs were studied by different research groups, caution needs to be exercised in interpreting the apparent differences in PCB profile.

For the Norwegian Sea, there is a few surface water PCB concentrations were available (see Table 1). Resulting subduction fluxes varied from 80 kg/year for PCBs (measured in 2004 by R. Lehmann et al., unpublished data, 2004) to 350 kg/year for PCBs measured in 2004 by Scholtz and Gage, 2004). With the data from Scholtz and Gage, (1998) being highest at 80 kg/year measured in 1991). As mentioned above, we consider these values to be free of uncertainties. In light of the extensive challenge in performing mass analysis at the pg level in the geosciences, the agreement by the different studies, using different sampling, extraction and analytical methods, is remarkable. While the data might represent a time-extend of declining PCB concentrations in the Norwegian Sea, the differences in concentration and trends are extrapolated fluxes are crucially influenced by inter-annual and geographical variability.

The uncertainty of knowing PCB concentrations in open ocean water is around a factor of 2 (looking at the 2001 and 2004 occurrence results). Thus, the uncertainty of the amount of PCBs removed, as the uncertainty of the deep-water formation is only around 13% in the North Atlantic and 30% in the N. Atlantic (Kennett, 2002). A comparison of subducted PCB fluxes ($F_{sub}$) versus the postulated PCB settling flux ($F_{set}$) due to the sinking organic carbon with PCBs attached shows the dominance of subduction in removing PCBs in all subduction regions (Figure 7). In all cases, the ratio $F_{sub}/F_{set}$ was highest for PCBs 28 and 52, with lower ratios for the other PCB congeners. For all congeners, in all regions, ratios were greater than 0, implying that organic carbon sinking fluxes were more important than the organic carbon settling fluxes on removing PCBs from the surface waters. The $F_{sub}/F_{set}$ ratios suggest that subduction is two to seven times more effective in removing PCBs from surface waters in the Norwegian, Ross and Weddell Seas than by carbon settling alone. Conversely, for the Labrador Sea, organic carbon sinking is only significantly higher than sinking fluxes for PCB congeners 28 and 52, whereas both removal mechanisms are similar in magnitude for the more hydrophobic congeners (Figure 2). This is the reason why high fluxes of organics carbon in the high productivity waters of the Labrador Sea. The higher importance of oceanic deep water formation for PCBs 28 and 52 relative to settling can be explained by their reduced affinity for organiccarbon, and thus lower bioconcentration potential in planktonic communities and sinking particles. In fact, there is a significant correlation between the $F_{sub}/F_{set}$ ratio and log $K_{oc}$ (taken from Benneker and Connell, 1983) in all four regions (data not shown). The correlations in the Labrador and Weddell Seas represent the lower and upper boundary, with $F_{sub}/F_{set} = -2.2 \log K_{oc} + 0.01$ and $F_{sub}/F_{set} = -1.8 \log K_{oc} + 0.03$, respectively.

[166] On the coast of the Atlantic Ocean, the four oceans deep water formation regions are calculated to remove about 870 kg/year of the PCB congeners considered here. This decrease is ca. 230 kg/year estimated to be removed due to the organic carbon settling flux within the same regions. We note that uncertainties in PCB concentrations will affect both $F_{sub}$ and $F_{set}$. Clearly, oceanic deep water formation results in removing additional PCBs from surface waters.
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and contributes an overlooked sink term in the Atlantic Ocean which is relevant at the regional scale. It has been shown that this global process can modify water and nutrient concentrations (Duchêne et al., 2002; Doan et al., 2004). Ozone depleting formation, which results in bather fluxes that these associated to etching particles, could also modify water and nutrient concentrations. The oceanic waters within the oceans where water mass modification occurs, it results from other processes from the surface mixed layer (Table 1). However, if we consider the importance of oceanic water mass formation (ca. 6.78 x 10^12 kg) versus carbon cycling (2 x 10^30), as estimated in previous

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Oceanic water mass formation, which results in bather fluxes that these associated to etching particles, could also modify water and nutrient concentrations. The oceanic waters within the oceans where water mass modification occurs, it results from other processes from the surface mixed layer (Table 1). However, if we consider the importance of oceanic water mass formation (ca. 6.78 x 10^12 kg) versus carbon cycling (2 x 10^30), as estimated in previous publications (Murphy et al., 2005, 2003), then the NPPs removed by subduction is relatively small.

Deep-ocean formation is not only a relevant mechanism to remove PTEs from surface waters, it also does not change the relative distribution of PCMs moved to the deep waters, this is in marked difference to PCE removal by carbon settling fluxes, where the different partitioning conversion is not the cause of PCMs from surface to deeper water masses (e.g., see Schrader et al., 2001). Finally, oceanic deep water formation is relatively more important for organic compounds that are more water-soluble (such as PTEs vs. PCE 126), on these compounds are less efficiently removed by carbon settling. This will also result in important subduction fluxes for other hydrophobic organic compounds, such as halogenated dioxines (HCB) and the halogenated polyaromatics (HAPs) (Stabentheiner et al., 1999, Schwert et al., 2001), however, at least in the case of HCBs, it is possible that other less processes such as bacterial degradation reactions could limit their persistence (e.g., Hansell et al., 1999, 2000).

All of these processes have been determined to be the major source of NPPs affecting the ocean water mass in the recent past and are key to the ocean's ability to maintain the oceanic NPPs as potential substrates for the extensive ocean surface water. As long as we are sufficiently sensitive to the ocean's point of view, we can be confident that these processes are the only ones that can affect ocean water mass formation.

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text for the \textit{Results and discussion} section of the article.
3.2.3.6 **Scientific contribution:**

*Atmospheric deposition of organic carbon to the oceans*

Jurado, E., Dachs, J., Duarte, C. M., Simó, R.
submitted to “Global Biogeochemical Cycles”

Jurado, E.: modelling of aerosol organic carbon fluxes, interpretation and writing  
Dachs, J.: modelling of gaseous organic carbon fluxes, interpretation and writing  
Duarte, C. M.: interpretation  
Simó, R.: support in the analysis of the dominant aerosol plumes
Results and discussion

ATMOSPHERIC DEPOSITION OF ORGANIC AND BLACK CARBON TO THE OCEANS

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Abstract

Atmospheric deposition of total organic carbon (OC), including gas-phase compounds, is lacking in most current models of the global carbon cycling. We present a pioneering methodology to estimate wet and dry deposition of total OC to the oceans, based on monthly satellite measurements and well known parameterizations for semi-volatile organic compounds. Furthermore, we discuss the potential importance and probable magnitude of diffusive exchanges of organic carbon. Distribution over the oceans show an important variability in atmospheric deposition fluxes due to a number of environmental factors such as temperature, productivity, wind speed, and higher marine-aerosol driven deposition. Global dry deposition of aerosol OC is estimated to be 14 Tg C y\textsuperscript{-1}, wet-particle and wet-
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Gaseous deposition are estimated 78 g C y$^{-1}$ and 187 g C y$^{-1}$, respectively. Furthermore, wet deposition fluxes due to their pulsed variability can be important locally and temporal sources of OC to the organic carbon. Finally, it is shown that the often neglected air-sea diffusive exchange fluxes of OC are predicted to be in the order of several thousands of 1 g C y$^{-1}$, and thus comparable to global net fluxes of CO$_2$. These figures show the important role that atmosphere-ocean exchange could play in the carbon cycle and the important spatial and temporal variability at different scales.

**Index terms:** Carbon cycling, organic carbon, atmospheric deposition, diffusive ocean-atmosphere exchanges

Introduction

The global carbon budget is a key node of the functioning of the Earth System affecting climate and its change, the global transport of pollutants and perturbations of biogeochemical cycles [Friedman, 2003; Jacobo, et al., 2004; Sarmiento, et al., 2004]. The global carbon budget is typically depicted by three compartments, land, ocean and the atmosphere, where land and ocean support fluxes of both inorganic and organic, but the atmosphere lacks organic carbon fluxes. The lack of organic carbon fluxes in the atmospheric compartment does not reflect a negligible role of atmospheric processes in these fluxes, but, rather, a current paucity of knowledge as to the organic carbon fluxes across the atmosphere. Indeed, the atmosphere is known to play a key role in several aspects of global cycling of organic compounds. The atmosphere is an efficient chemical reactor, responsible for major oxidative losses of organic compounds due to OH radicals and O$_3$. Furthermore, since atmospheric transport is fast in comparison to oceanic transport, it is an efficient medium for redistributing chemicals at regional and global scales [Jawo, et al., 1993].

The exchange of carbon in its oxidized form (carbon dioxide) has received major attention by the scientific community, yielding hundreds of thousands of measurements of CO$_2$ disequilibria between
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surface waters and the lower atmosphere, which have allowed to estimate the global atmosphere-ocean exchange of CO₂ with uncertainties below 20%. This contrasts with the poor knowledge available on the significance and magnitude of atmosphere-ocean exchange of reduced carbon at regional and global scales, especially in the form of organic carbon. Indeed, estimations of regional and global exchanges between the atmosphere and the ocean are only available for few organic compounds that are of concern for their toxicity [Yamada et al., 2004; 2005] or of interest for their biogeochemical significance, e.g., [Jaehn et al., 2010; Niiyama and Dutra, 2002].

Atmospheric deposition of organic carbon can occur by: i) dry deposition of aerosol bound organic compounds, ii) diffusive air-water exchange of gas phase organic compounds and iii) wet deposition due to precipitation scavenging of gas and aerosol phase organic compounds. Until recently, the only measurements available were those related to wet deposition [Raymond, 2000; Willey et al., 2000]. Willey and coworkers by reviewing measurements of the non-purgeable dissolved organic carbon in rain water reached a global estimation of dissolved organic carbon inputs of 400 Tg C y⁻¹, of which 90 Tg correspond to wet deposition to the ocean. This figure is significantly higher than global estimates from models based on emission inventories (IPCC, 2001). However, other authors have reported higher DOC concentrations in rain water [Raymond, 2005] than those considered by Willey. Other available, indirect estimates of dry deposition of aerosol bound OC at regional and global scales are reported elsewhere [de Madron et al., 2003; del Giorgio and Duarte, 2007], and aerosol-bound organic carbon inputs have been recently reported for the NE Subtropical Atlantic [Duarte et al., 2006], but none of these account for depositional fluxes associated to gas-phase organic compounds. Yet a comprehensive estimation of deposition of aerosol bound OC to the global oceans, other than based on emission inventories, is lacking. Indeed, most global burdens are obtained from transport models, but they are highly dependent on the veracity of the emission inventories [Cooke and Wilson, 1996; Wang, 2004].
More surprising is that until recently, there was not a single estimation of the magnitude and relevance of the diffusive exchanges of organic carbon between the atmospheric gas phase and the marine dissolved phase. Yet, the knowledge available for some individual volatile organic compounds such as methanol, acetone, or semi-volatile organic compounds such as polycyclic aromatic hydrocarbons and polybrominated biphenyls suggests that most of the total deposition of organic carbon must be due to diffusive exchanges. A recent study by Dachs et al. (2005) suggests that these diffusive exchanges are large in magnitude, very dynamic and important for the regional carbon budget of the Nl. Atlantic.

The objectives of this study are: i) to provide the first comprehensive estimation of the global dry and wet deposition of aerosol bound organic compounds, and ii) to examine the potential importance of diffusive exchanges of organic carbon between the atmosphere and the ocean. The estimates presented here are obtained by combining satellite measurements of a number of variables with field measurements of aerosol concentrations and measurements. This is thus a novel approach to estimate global burdens of aerosol carbon, based on determining the dominant aerosol type over the oceans from remote sensing parameters.

Model development and data sources

Parameterization of atmospheric deposition fluxes. Atmospheric depositional fluxes of aerosol carbon, namely dry aerosol deposition and wet particle deposition, have been parameterized using the methodology previously developed for individual organic compounds, such as persistent organic pollutants (POPs) [Jarosz, et al., 2004, 2005]. POPs are hydrophobic organic compounds, therefore, with high affinity for aerosol organic carbon. Thus the dynamics of POPs and OC are similar.
Fluxes of dry aerosol deposition of organic and black carbon aerosol ($F_{\text{org, dry}}$ and $F_{\text{BC, dry}}$, mg m$^{-2}$ d$^{-1}$, respectively) are estimated as the product of organic/black carbon aerosol-phase concentration ($C_{\text{org}}$, and $C_{\text{BC}}$, mg m$^{-2}$, respectively) and the dry deposition velocity of the depositing particle ($v_{\text{dry}}$, m d$^{-1}$) [Baker and Hites, 1999]:

\[ F_{\text{org, dry}} = v_{\text{dry}} C_{\text{org}} \]  
\[ F_{\text{BC, dry}} = v_{\text{dry}} C_{\text{BC}} \]  

Then the total carbonaceous dry aerosol deposition flux ($F_{\text{dry}}$) is the sum of $F_{\text{org, dry}}$ and $F_{\text{BC, dry}}$. On the other hand, wet particle deposition flux (\(F_{\text{wet, dry}}\) and \(F_{\text{wet, BC}}\), mg m$^{-2}$ d$^{-1}$) is given by [Hilderman, 1986]:

\[ F_{\text{wet, dry}} = p_{\text{p}} W \cdot C_{\text{dry}} \]  
\[ F_{\text{wet, BC}} = p_{\text{p}} W \cdot C_{\text{BC}} \]

where $p_{\text{p}}$ is the precipitation rate (m d$^{-1}$) and $W$ is the particle washout ratio (dimensionless).

Both $v_{\text{dry}}$ and $p_{\text{p}}$ have been derived from climatological monthly mean satellite products of resolution of 1°×1°, which cover the global oceans and allow to assess the spatial and temporal variability. The parameter $v_{\text{dry}}$ is dependent not only on atmospheric turbulence (as influenced by wind speed), but on the aerosol size. For this purpose it has been necessary to assume a single lognormal distribution for the number concentration of aerosols, divide the aerosol population into size intervals, use aerosol optical parameters to derive the volumetric fraction of interval, and to apply widely used parameterizations [Slan and Slan, 1980, Williams, 1982] in order to obtain the deposition velocity of
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Each midpoint nine interval. A detailed explanation of the methodology is reported in [Jimeno, et al., 2004].

On the other hand, particulate washout (Wa) has been assumed constant and equal to 2 10^{-7}. This value has been adopted in various modeling exercises for semivolatile organic compounds [Jimeno, et al., 2005; Mackey, et al., 1988]. A detailed discussion of this parameterization is also found in [Jimeno, et al., 2004].

**Estimation of aerosol OC and BC concentrations**: The global distribution of aerosol carbon concentration, i.e. C_{P,OC} and C_{P,BC}, is an important feature to resolve. Measured concentrations showed high variability, contributed by the important inherent variability (see supplementary material) of the aerosol distributions and the important biases in current measurement techniques [Kinne, et al., 2003]. In addition, there is a significant paucity of measurements in the southern hemisphere.

Therefore, a simple extrapolation from the available measured concentrations to obtain a global coverage over the oceans seems inappropriate, even less if temporal variability is to be addressed. Instead we have obtained the carbonaceous concentrations over the oceans from remote sensing data.

As starting point we have used the following expression:

\[
\begin{align*}
C_{P,OC} &= \text{TSP} \cdot f_{OC} \\
C_{P,BC} &= \text{TSP} \cdot f_{BC}
\end{align*}
\]

where \( f_{OC} \) and \( f_{BC} \) are the unitary mass fraction of organic and black carbon, respectively, in the aerosol (gC gTSP^{-1}), respectively, and TSP (mg m^{-3}) is the average total suspended matter in the atmospheric boundary layer (ABL). TSP has been obtained by applying an algorithm recently developed by Gasso and Hegg [2003] to optical properties given by MODIS sensor, assuming that the mass concentration of aerosols in the ABL (assumed to be 1 km) doubles that in the free troposphere.
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Although δ and ω are strongly dependent on the aerosol source and type, examining various literature sources and accounting for the satellite retrieved parameters, we have considered six main categories of aerosols: biomass burning, urban and suburban aerosol -mainly due to industrial emissions-, dust, sea-salt (also termed marine aerosol), continentally influenced air masses in the distant marine atmosphere and baseline background aerosol. Each one of these aerosol types have a characteristic δ and ω for their submicron and supermicron aerosol (Table 1). For dust and sea-salt we have just considered the supermicron aerosol; precisely this was an assumption made in the definition of these kinds of aerosol in the present study. It is easily noticed that major fractions of the organic and black carbon are assumed to be found with the submicron sizes. Maximum percentages are found in industrial emissions and fine biomass burning aerosols emitted from vegetation fires.

The spatial distribution of the dominant aerosol type from satellite observations has been approximated by determining thresholds to widely used satellite measures: aerosol optical depth (AOD), its variability (σAOD), the fraction of small aerosols (η), wind speed distributions (uw) and fire counts. A look-up table (Table A1.1, in the supporting material) was then elaborated, based on published sources and previous basic knowledge of aerosol spatial and seasonal distributions [Brasseur, et al., 2003; Heinzenberg, et al., 2000; Hostetler, et al., 1997; Kingman, et al., 2001; Kingman, et al., 2002; Smirnov, et al., 2002; Tétoir, et al., 2003]. A detailed explanation of the reasoning and hypotheses used, as well as maps of the modeled aerosol distributions at monthly scale are reported in the supporting information.

Results and Conclusions

Aerosol organic carbon concentrations and validation: Monthly averages of the global distribution of COC and COC (Fig. 1) were obtained combining equation 3 and the distribution of the dominant
aerosol type (presented in the supplementary material). In order to validate these results we have performed a comparison between a comprehensive number of published measurements from coastal stations research cruises, aircrafts and sunphotometers and our estimated \( C_{P,SK} \) and \( C_{P,MB} \) (see Table A2 in supplementary material). Estimated \( C_{P,SK} \) and \( C_{P,MB} \) agreed with measurements in the northern hemisphere within a factor of 3 in most cases, but tend to overestimate southern hemisphere OC and BC concentrations (Fig. 2), where coarse sea-salt plays a major role (see Figure A1.1 in supplementary material). Indeed, the load of organic matter in the sea-salt aerosol in the remote marine aerosol remains still uncertain [IPhadelph, et al., 2004; Stinner, et al., 2004]. The overestimation of southern hemisphere measurements may partially be apparent, as the measured aerosol samples have a large vertical and temporal variability and may not be fully representative of the sea-salt concentrations in the lower atmosphere, which is the relevant property estimate the deposition of carbon to the oceans.

**Dry deposition of aerosol OC to the global oceans:** The modeled dry deposition fluxes of OC aerosol to the global oceans showed a ten fold geographical variability (Fig. 3). Modeled fluxes were higher in the areas with high aerosol OC concentrations (see Figure 1), and where environmental conditions, such as larger aerosol size and high wind speed, are conducive to enhanced dry deposition velocities. Indeed fluxes tend to be high at high latitude regions, where wind speed is higher, and in dust influenced areas. Even though dust has a low OC content (see Table 1), its large aerosol size and relatively high wind speeds in trade winds regions do result in relatively high depositional fluxes, consistent with recently reported measurements [Duch, et al., 2005]. Fluxes are especially important in areas with high concentrations of sea salt, due to the scavenging role of this on organic compounds near the sea surface, as has been suggested for individual organic compounds [Juras, et al., 2004]. The results shown here and previous reports of relatively high concentrations of OC in marine aerosols [Caro, et al., 2004; Monahan and Dom, 2001], together with growing evidence of the important contribution of biogenic OC in marine aerosols [ODowd, et al., 2004], points out to the important role