that they may play in the lower atmosphere, an issue that requires further research. Conversely, OC dry aerosol deposition is especially low in the middle of the oceanic gyres.

Table 2 shows the average and yearly accumulated OC dry deposition fluxes to the global oceans for latitudinal bands. It should be noted that the yearly accumulated fluxes is the sum of each of the climatological means. The global OC dry deposition flux is of 14 t g C y⁻¹, with a major contribution of the 30°-60° latitudinal band. This flux is more than 100 times smaller than the net CO₂ exchange between the atmosphere and the ocean [Fletcher et al., 2006; Takahashi et al., 2002]. Even small, an important fraction of aerosol OC appears to be effectively transferred to deep waters and oceanic sediments as is ubiquitously shown by the molecular signals in settling particles and sediments [Leblanc et al., 1987; Wakeham et al., 1991]. The relatively low global aerosol OC flux to the ocean may explain the neglect of atmospheric deposition of OC despite unambiguous molecular fingerprints identifying these materials in sediments.

However, it is well known that dry aerosol deposition of organic compounds, although eventually important locally or regionally, represents a small fraction of the total atmospheric deposition of organic compounds [Girolami et al., 2007; Jarvis, et al., 2005]. This is so widely accepted in either the literature of organic volatile and semi-volatile compounds, that this component of the flux is often assumed to be negligible and not quantified [Dachs et al., 2007]. Therefore, a reliable assessment of the global atmospheric OC deposition to the ocean must extend beyond the flux associated to aerosols to estimate the global wet and diffusive deposition of OC.

**Wet deposition of aerosol OC to the global oceans:** Wet deposition does scavenge aerosols and gas-phase compounds, therefore it is necessary to consider both contributors to the total wet deposition flux. Aerosol scavenging of aerosol OC and BC is estimated here using equation 2 as explained above. Figure 4a shows the global distribution of wet deposition of aerosol OC for a representative month and table 2 shows the average and accumulated fluxes for latitudinal bands. These fluxes follow the
variability of aerosol OC concentration, but especially of precipitation rates. Therefore, it is clear that higher fluxes are found in the intertropical area and high latitudes where annual precipitation is more than 10 fold that of other regions. It should be commented that rain water scavenging of aerosols is very effective, and that a rain event can remove most of the aerosols in the atmospheric boundary layer and contribute with a pulse input of OC, and other elements, to the ocean. It has been reported that these inputs can fuel bacterial productivity [Schindler and Sanders, 1999] and thus have an important impact on oceanic processes. This contrast with dry particulate OC inputs, that even though can also have a pulsing nature, rank well below in magnitude to the inputs associated with intense rain events.

Concerning black carbon, Table 2 shows the average and accumulated estimated dry and wet aerosol deposition. Black carbon deposition is 15% of that of organic carbon and about 2 1g C y^-1 and 11 1g C y^-1 for dry and wet aerosol deposition. The total depositional flux is much higher than the values of 0.17 - 0.32 1g C used in current global transport models of aerosol BC [Loeke and Wilkin, 1996; Wang, 2004]. The discrepancy between these and present estimates could be caused by the different approaches used, since the models were based on emission inventories and constant dry deposition velocities, and thus not accounting for the large temporal and spatial variability in deposition fluxes. However, the total aerosol input derived here is similar, or slightly lower, than the total emission estimation of BC, i.e. 14 Tg C y^-1 [Léonsse, et al., 1996].

The global particulate OC wet deposition flux is calculated to represent 78 Tg C y^-1. This figure is within the range of the back of envelope estimation (70-79 Tg C y^-1) made by Dove et al. [1991] two decades ago. Together with the dry deposition flux of OC it results in an input of 97 Tg C y^-1, within the same order of magnitude as the global emission estimate of 106 Tg C y^-1 of aerosol OC [Léonsse, et al., 1996], which was the best available estimate until the recent work by Willey et al. [2000]. These authors arrived to an estimate of 90 Tg C y^-1 for total wet deposition, including dissolved and particulate OC from rainwater. It is difficult to estimate which fraction of Willey’s et al. estimation is due to particulate wet scavenging. Even though particulate OC only made 10-15 % of total rainwater
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OC, aerosol OC could also be transfer to the dissolved phase during scavenging. This leads to the consideration of the magnitude of wet deposition of total gas phase organic compounds which has not yet been attempted for total organic carbon, but has been done for some individual organic compounds [Haberk and Hites, 1999; Jurado, et al., 2003]. Indeed, the estimate reported by Willey et al. points out the potential magnitude of wet gaseous depositional fluxes, but should be regarded as a lower estimate of wet depositional fluxes since the analytical method used for estimated OC in rainwater concentrations did not take into account the volatile and semivolatile compounds. Willey et al. estimate of wet deposition fluxes were based on measurements of the non-purgeable OC rainwater content, where purgeable (most volatile and semivolatile) organics are lost during the purging step before the sample enters the U analyzer. Furthermore, other studies have reported higher OC concentrations in rainwater [Raymond and Harley, 2001].

There are indeed important gaps in our understanding of the atmospheric composition in terms of organic compounds, since a comprehensive inventory of gas phase OC is still not available and there are high uncertainties also on abundance of OC aerosols in some atmospheric regions. However, there is an emerging body of estimates and other lines of evidence that points to an important role of gas phase organic compounds in the biosphere, and especially in atmospheric deposition fluxes [Hudib, et al., 2005, Heidt, et al., 2005].

Wet gaseous deposition of OC to the global oceans. The potential for a chemical to be volatilized or exchanged between the gas-phase and water depends on the ratio of vapor pressure and water solubility at equilibrium. This ratio is also the Henry’s law constant (H). During the process of scavenging, raindrops are evidently in contact with air and therefore there is an equilibration of gas phase OC (GOC) with exchangeable dissolved phase OC (EDOC). Not all the dissolved organic carbon (DOC) can be volatilized or exchanged with the gas phase. Indeed, significant fractions of DOC are high molecular weight chemicals, or ionic chemicals with extremely low H° values.
Therefore, total DOC is made of exchangeable DOC (or E-DOC) and non-exchangeable (or non-purgable) DOC. At equilibrium, the dimensionless Henry’s law constant (H) gives the ratio of concentrations of GOC and E-DOC (GOC_{eq}/H = E-DOC_{eq}). In fact, H is used to estimate wet deposition of organic compounds from their gas phase concentrations [Juddiman, 1988; Jurado, et al., 2005], and in the present work wet deposition of gas phase organic carbon can also be estimated by assuming this gas phase-rainwater equilibration of organic compounds.

Gaseous wet deposition fluxes of organic carbon (F_{W,G,O,C}, \text{mmol m}^{-2} \text{d}^{-1}) are then given by:

\[ F_{W,G,O,C} = \frac{F_{OC}}{H} \]  \hspace{1cm} [4]

At sea-level, the only reports of GOC/H values are those of Itahara et al. (2003) that recently showed that the gas phase OC concentration (GOC) after equilibration with water resulted in dissolved OC concentrations ranging from 10 \text{ M} \text{C} to more than 100 \text{ M} \text{C}, for the NE Atlantic ocean, with average values of 40 \text{ M} \text{C} for the open ocean, and with small seasonal variability. These figures are the best estimations available for dissolved phase concentrations of OC equilibrated with air over the oceans and thus here wet deposition over the atmosphere has been estimated using a rainwater concentration of GOC/H of 40 \text{ M} \text{C}, however, this estimation may have an uncertainty of a factor of 2 that will be transferred to the final deposition estimations. Figure 4b shows the predicted wet deposition fluxes due to gas scavenging for a representative month. The spatial variability here, due to the assumptions made, follows basically the spatial variability of precipitation rates. Table 2 shows the average and accumulated fluxes for latitudinal bands. Globally, the predicted gas phase wet deposition flux is of 100 \text{ I} \text{g} \text{C} \text{y}^{-1}. If this estimate is considered together with the particulate wet deposition flux of OC, we get a total wet deposition flux of OC of 265 \text{ I} \text{g} \text{C} \text{y}^{-1}, this is about 15% of estimated net CO$_2$ diffusive fluxes [Fletcher, et al., 2008b; Takahashi, et al., 2002], and 20 times higher than was has been estimated here as a dry particulate flux of OC, a ratio consistent with current knowledge of deposition of organic
compounds to the oceans [Broecker, et al., 2000]. The estimate of 265 ± 1 g C y\(^{-1}\) is 2.6 and 2.2 times higher than those given by Willey et al. [2000] and Raymond [2005], but the estimations of these authors are lower-end estimations since they consider based on non-purgeable DOC measurements exclusively. In fact non-purgeable DOC is what has been usually measured when DOC is reported in the literature, and it does not account for the potential contribution of purgeable organic compounds to the total OC inventory.

In order to assess the uncertainty associated to these predictions of wet deposition fluxes, a comparison/validation is done with the reported measurements. Indeed, there are now a number of available reports on OC concentrations in rainwater. However, the interpretation of these measurements is not so evident, since most may contain still some fraction of LDOC as discussed above. Here a comparison of reported DOC and estimated DOC is given in table 3. Measures are highly variable, affected by the method employed (purgeable, non-purgeable) and by the redissolution of particulate organic carbon to the dissolved phase. In broad terms modeled estimates agree with measured ones within a factor of 3 or better.

Is diffusive atmosphere-ocean exchange of OC relevant at the global scale? Even though several reports have pointed out to the necessity of measurements and predictions of diffusive exchanges of total OC between the atmosphere and the ocean [Duce and Murnane, 1977, Willey, et al., 2000], this has been omitted so far. Recently, Dachs et al [2005] has shown that diffusive fluxes of OC are important in the N.E. Subtropical Atlantic and should be taken into account in regional marine carbon flux mass balance. At this point the empirical basis available is insufficient to derive a robust estimate of the actual global atmosphere-ocean exchange of OC, comparable to that produced for CO\(_2\) [Tokosha, et al., 2002]. However, it is possible to assess the possible orders-of-magnitude of these fluxes, thereby assessing their potential importance for the carbon budget of the oceans.
The diffusive air-water exchange of OC ($f_{\text{AW,OC}, \text{mmol m}^{-2} \text{d}^{-1}}$) is given by:

$$f_{\text{AW,OC}} = k_{\text{AW}} \left( \frac{\text{DOC}}{H^+} \right)$$

[5]

Where $k_{\text{AW}}$ is the air-water mass transfer coefficient and is estimated in the usual manner [Nightingale et al., 2000]. The first term of equation 5 is the gross volatilization flux, and the second term is the gross absorption flux. The direction of the net diffusive fluxes will be given by the addition of these two fluxes. It is possible to obtain global fields of $k_{\text{AW}}$ values following the methodology described elsewhere [Dachs et al., 1999]. In order to obtain a conservative estimate of the order of magnitude of these fluxes, we can assume that the air-water gradient is small compared to the concentrations of OC in the gas-phase and dissolved phase. As commented above, GOC/H+ concentrations are higher than 10 $\mu$M and average 40 $\mu$M for the tropical Atlantic. Conversely, oceanic concentrations of non-purgeable (non volatile) DOC range between 60 $\mu$M in polar waters to more than 100 $\mu$M in coastal waters, being 70 $\mu$M a representative figure for most oceanic waters [Kirstegart et al., 2002].

Concerning the purgeable or exchangeable DOC, recently, Dachs et al. [2005] reported average EDOC concentrations of 35 $\mu$M for the NE Atlantic but with an important spatial variability, specially in coastal areas. As a conservative approach, we have assigned a lower estimate for the gradient of exchangeable OC between the atmosphere and the ocean (EDOC-GOC/H+) of -1 $\mu$M, which is five times smaller than that reported by Dachs et al. [2005] and would indicate that the air-water gradient of exchangeable OC is somewhat above 1% of oceanic DOC. Figure 5 shows the calculated fluxes derived by multiplying the $k_{\text{AW}}$ values by a EDOC-GOC/H+ gradient of -1 $\mu$M. There is a high spatial variability that is mainly due to the non-linear influence of wind speed on diffusive fluxes [Livingstone and Imboden, 1993], and temperature on diffusivities. For most of the oceanic regions, with the exception of areas with high wind speeds, the fluxes given are of the same magnitude or two fold.
higher than net fluxes reported for CO$_2$ in the southern hemisphere and other high wind speed regions
the diffusive CO fluxes are significantly higher. The global direction of this flux can not be elucidated here, since some oceanic regions can be a source to the atmosphere and others a sink, as suggested by
reports for the NE Atlantic [Duels et al., 2005]. However, as exercise, if the fluxes given in figure 3 are
summed up, a global flux of 4400 Tg C yr$^{-1}$ is obtained which is more than two fold higher than that predicted for atmosphere ocean exchange of CO$_2$. It is impossible here to constrain this
conservative flux estimate further, but the figures given here confirm the urgency for trans-regional
assessment of air-water diffusive fluxes of organic carbon and its role in the regional and global carbon
cycle.

Acknowledgments

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Table 1: Characteristic organic carbon and black carbon aerosol content for each one of the considered aerosol types.

<table>
<thead>
<tr>
<th>Aerosol type</th>
<th>f_{OC} (%)</th>
<th>f_{BC} (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Biomass burning</strong></td>
<td>19.1</td>
<td>15.3</td>
<td>submicron aerosol</td>
</tr>
<tr>
<td></td>
<td>3.8</td>
<td>0.6</td>
<td>supermicron aerosol</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>6.3</td>
<td>submicron aerosol</td>
</tr>
<tr>
<td></td>
<td>31.9</td>
<td>1.4</td>
<td>supermicron aerosol</td>
</tr>
<tr>
<td><strong>Industrial emissions</strong></td>
<td></td>
<td></td>
<td>[Brasseur, et al., 2003]</td>
</tr>
<tr>
<td><strong>Dust</strong></td>
<td>1.5</td>
<td>0.5</td>
<td>supermicron aerosol</td>
</tr>
<tr>
<td><strong>Sea-salt</strong></td>
<td>1.7</td>
<td>0.1</td>
<td>supermicron aerosol</td>
</tr>
<tr>
<td>Continuously influenced</td>
<td>13.7</td>
<td>1.2</td>
<td>submicron aerosol</td>
</tr>
<tr>
<td></td>
<td>2.2</td>
<td>0.5</td>
<td>supermicron aerosol</td>
</tr>
<tr>
<td><strong>Background aerosol</strong></td>
<td>18.5</td>
<td>1.9</td>
<td>submicron aerosol</td>
</tr>
<tr>
<td></td>
<td>4.3</td>
<td>0.9</td>
<td>supermicron aerosol</td>
</tr>
</tbody>
</table>
Table 2: Global yearly averaged and accumulated fluxes of organic carbon (OC) and black carbon (BC). (Dry deposition: F_{dry}, Wet particle deposition: F_{w,d}, Wet scavenging deposition: F_{w,s} )

<table>
<thead>
<tr>
<th>Latitudinal Bands</th>
<th>Average [mg m(^{-2}) d(^{-1})]</th>
<th>Accumulated [Tg year(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(F_{\text{OC, dry}})</td>
<td>(F_{\text{OC, wet}})</td>
</tr>
<tr>
<td>60N-80N</td>
<td>0.19</td>
<td>0.03</td>
</tr>
<tr>
<td>30N-60N</td>
<td>0.16</td>
<td>0.02</td>
</tr>
<tr>
<td>0-30N</td>
<td>0.12</td>
<td>0.02</td>
</tr>
<tr>
<td>30S-0</td>
<td>0.10</td>
<td>0.01</td>
</tr>
<tr>
<td>60S-30S</td>
<td>0.14</td>
<td>0.01</td>
</tr>
<tr>
<td>90S-60S</td>
<td>0.22</td>
<td>0.03</td>
</tr>
<tr>
<td>TOTAL</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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## Results and discussion

### Table 3: Comparison between DOC measured in island and coastal sites and estimated in this study

<table>
<thead>
<tr>
<th>Source</th>
<th>Location</th>
<th>(lat,lon)</th>
<th>Modeled DOC (µM)</th>
<th>Measured DOC (µM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Raymond, 2005]</td>
<td>New Haven CT, coastal</td>
<td>(41N, 73W)</td>
<td>102</td>
<td>52</td>
</tr>
<tr>
<td>Mean ± SE</td>
<td></td>
<td>(13N, 117W)</td>
<td>80</td>
<td>24</td>
</tr>
</tbody>
</table>
Figure Legends

1- Global distribution of aerosol organic carbon for June and November 02-04.
2- Comparison of measurements and predictions of aerosol organic carbon and black carbon. Also a map indicating the location of measurements is shown (cross: sampling site, rectangle: spatial coverage campaign).
3- Global distribution of dry aerosol deposition of organic carbon for November 07-04
4- Global distribution of wet deposition of organic carbon for November 07-04. Results for wet deposition of aerosol OC (fig. 4A) and gas-phase OC (fig. 4B) are shown separately.
5- Estimation of global diffusive air-water exchange of organic carbon assuming a gradient in exchangeable OC concentrations of 1 μM (EDOC-OC/H = 1 μM).
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Figure 1.

$C_{P, OC}$ June 02-04

$C_{P, BC}$ November 02-04

$[\mu g C m^{-2}]$ $[\mu g C m^{-2}]$
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Figure 2:

[Graphs showing data analysis and field measurements]
Figure 3

$F_{\text{DO$_3$ OC}}$ November 02-04

$[\text{mg C m}^{-2} \text{ d}^{-1}]$
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Figure 4:

$F_\text{WD P OC}$ November 02-04

$F_\text{WD G OC}$ November 02-04

[mg C m$^{-2}$ yr$^{-1}$]

[mg C m$^{-2}$ yr$^{-1}$]
Figure 5:

F_{AW,OC}  November 02-04

[mg C m^{-3} d^{-1}]
SUPPLEMENTARY MATERIAL for “ATMOSPHERIC DEPOSITION OF ORGANIC AND BLACK CARBON TO THE OCEANS”

ANNEX 1: Methodology to derive aerosol climatologies

Annex 1 aims to explain the methodology used to obtain global distribution of the dominant aerosol type over the oceans, inferred from satellite measurements.

We have considered 6 categories of aerosols over water masses: biomass burning (BB), urban and suburban aerosol (IN) - mainly due to industrial emissions, dust (DU), sea-salt (SS) - also termed marine aerosols, continentaly influenced air masses in the distant marine atmosphere (BK1) and baseline background aerosol (BK2). We have established those categories because they have significantly different organic and black carbon fractions (fOC, fBC) and can be determined quite easily from remote sensing measures. The corresponding fOC and fBC values are reported in the main manuscript (Table 1). They are referred to averaged typical air-masses in the Atlantic.

The classification procedure is mainly based on satellite measurements that are proxies for the amount and sort of aerosol: aerosol optical depth (AOD), which describes the attenuation of sunlight by a column of aerosol, its standard deviation ($\sigma_{AOD}$), indicative of the AOD variability, and the fraction of optical depth corresponding to submicron aerosol ($\eta$, [0 1]). Furthermore, wind-speed distributions referred to 10 m above the surface of the sea ($u_10$, m s$^{-1}$), fire-counts, LGM3 land cover classification map, all derived from satellite measurements were used. All parameters constitute monthly means, have a resolution of 1° x 1° and correspond to climatological averages of three consecutive years (2007-2009). More concretely, AOD, $\sigma_{AOD}$ and $\eta$ have been obtained from the Moderate-Resolution Imaging Spectroradiometer Instrument (MODIS, http://modis.gsfc.nasa.gov); $u_{10}$ from the NOAA special sensor microwave imager (SSM/I, http://www.nco.nesdis.noaa.gov/oa/satellite/ssm/); fire-counts determined from nighttime ATSR
data as the times de 3.7 m channel exceeds 308 K, reported in the World Fire Atlas from the European Space Agency (http:// Chap. 38.1.3 (http:// Chap. 38.1.3, the urban centers map from IGBP land cover classification (http:// Chap. 38.1.3). Thresholds are then determined (see table A1.1) using as well bibliography sources [Broux et al., 2003, Husar et al., 1997, Kaufman et al., 2001, Kaufman et al., 2002, Smirnov et al., 2002, Tegen et al., 1997] and knowledge of aerosol spatial and seasonal distributions. The following assumptions have been taken into account: dust is the major contributor to AOD, followed by biomass burning, biomass burning aerosols and industrial emissions are dominated by fine aerosol, instead dust and seasalt are dominated by coarse aerosol, active fires have been used as proxies for biomass burning emissions [Rossetti et al., 2004, Generoso et al., 2003] seasalt particles correlate with high winds, background aerosol is stable spatial-temporally. By means of simplification, common thresholds for all the oceans have been considered and diurnal variability is not accounted since we use monthly averages of satellite data. Finally, Arctic Ocean has not been treated separately as a single category, even if it has differential characteristics, because we focus the study in temperate areas, where most measures are obtained.

Table A1.1: Look-up table: allows to obtain the spatial distribution of dominant aerosol type over the oceans

<table>
<thead>
<tr>
<th>Dominant aerosol type</th>
<th>AOD</th>
<th>σ_0.5</th>
<th>η [μm]</th>
<th>u_{10} (m s^{-1})</th>
<th>Other conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass Burning (BD)</td>
<td>≥ 0.7</td>
<td>≥ 0.6</td>
<td></td>
<td></td>
<td>Proximity to Fire-Points (ATSR World Fire Atlas)</td>
</tr>
<tr>
<td>Industrial emissions (IN)</td>
<td>Dust (DU)</td>
<td>0.1 – 0.7</td>
<td>≥ 0.6</td>
<td>&lt; 0.6</td>
<td>Proximity urban centers (IGBP land cover classification map) No BB No BB, No IN</td>
</tr>
<tr>
<td>Seasalt (SS)</td>
<td>≥ 0.4</td>
<td>&lt; 0.5</td>
<td>&gt; 8</td>
<td></td>
<td>Distance from coast No BB, No IN, No DU</td>
</tr>
<tr>
<td>Continuously influenced (BB1)</td>
<td>≥ 0.075</td>
<td></td>
<td></td>
<td></td>
<td>No BB, No IN, No DU, No SS</td>
</tr>
</tbody>
</table>
Applying look-up table A1.1 we obtain typical aerosol climatologies for each averaged month of 2002-2004. In each 1x1 degree of resolution we consider the characteristics of the dominant aerosol on the mass concentration.

Figure A1.1:

The reported methodology, based on monthly satellite global products, provides rough pictures of the seasonal variability and distribution of the typical aerosol climatologies that agree with observations and modeling exercises [Brasseur et al., 2003; Chu et al., 2004; Chu et al., 2003; Duncan et al., 2003; Husar et al., 1997; Johansen et al., 2000]. From Fig. 1, a seasonal variability is seen in almost in every region, with the exception of the very remote oceanic...
regions. On the other hand, the Southern Hemisphere is relatively uninfluenced by continental sources, instead anthropogenic emissions are mainly located in mid-latitudes of the Northern Hemisphere. Maximums of biomass burning emitted aerosols occur in the tropical Atlantic close to Africa, and it peaks in the end of dry season. Other regions of intense biomass burning are Indonesia, Central South America and boreal forests of Asiatic Russia and Canada. On the other hand, it is easy to distinguish the Saharan plume of dust that goes from West Africa to Central America, and which is most intense during the warm seasons, from March to August. Other dust plumes, like the dust outflow from Northern Asia, are also highly seasonal. The high backscatter of whitecaps in Southern Ocean make difficult the characterization of the dominant aerosol and create confusion between dust and sea-salt aerosol. This typology of aerosol, sea-salt, is produced by mechanical disruption of the sea surface and is a major component over the water masses. It tends to be predominant with higher wind speeds, as encountered in mid-high latitudes.
3.2.3.7 Major issues and conclusions of chapters 3.2.3.2 - 3.2.3.6

- Remote sensing of biogeophysical data is useful to estimate the mass transfer coefficients of POP processes.

- There is an important spatial and seasonal variability of the atmospheric depositional fluxes, especially noteworthy for the wet deposition fluxes. It is clearly important to consider spatially resolved data for global assessment of POP cycling instead of limiting the study to the mean values. In this context the use of remote sensing data is greatly justified.

- The total dry deposition of $\Sigma$PCBs and $\Sigma$PCDD/Fs to the Atlantic Ocean is estimated to be $2200 \text{ kg year}^{-1}$ and $500 \text{ kg year}^{-1}$ respectively, while the wet deposition is $4100 \text{ kg } \Sigma$PCBs year$^{-1}$ and $2500 \text{ kg } \Sigma$PCDD/Fs year$^{-1}$ and the net air-water exchange is $22000 \text{ kg } \Sigma$PCBs year$^{-1}$ and $1300 \Sigma$PCDD/Fs year$^{-1}$. The comparison of estimated values and measured fluxes gave good results, a factor between 1 and 2 for wet deposition.

- By comparing the mass transfer coefficients of each flux we obtain the dominant flux at a global scale. They show the tendency for a contaminant to deposit either via dry aerosol deposition, gaseous absorption to ocean surface or via rain scavenging, independently of the actual POP occurrence.

- PCBs, which are found mainly in the gas phase, are primarily introduced into the ocean water surface by gaseous absorption almost everywhere. PCDD/Fs show a higher affinity to aerosols. Hence, for these compounds, either wet or dry deposition is the dominant process in some oceanic regions. It should be stressed the importance of particle deposition mechanisms by marine aerosol in high latitudes of. Furthermore dominance of wet deposition fluxes is clearly marked in the Intertropical Convergence Zone (ITCZ), and on a short-term basis it has a dramatic effect.

- Oceanis deep-water formation is regionally a major transport mechanism. Indeed, in the main deep-water water formation regions (Norwegian Sea, Labrador Sea, Weddell Sea and Ross Sea), removal of PCBs by subduction of surface waters exceeds the removal due to settling of particles. However, on a global scale, settling is greater.

- It has been developed a simple and effective method based on the analyzed dynamics of POPs to obtain global maps of aerosol organic carbon deposition to the global oceans. Indeed the deposition of organic and black carbon results only dependent on satellite measurements. Also, parameterizations of wet gaseous and air-water diffusive fluxes of
total organic carbon have been implemented at the global scale, the latter indirectly evaluated as ratio \( \frac{C_{\text{GOC}}}{H'} \), where \( C_{\text{GOC}} \) is the gaseous organic carbon (Dachs et al., 2005).

- The estimated organic carbon and black carbon concentrations, necessary to assess the depositional fluxes, agree with measurements in the northern hemisphere within a factor of 3 in most cases, but tend to overestimate southern hemisphere, where coarse sea-salt plays a major role. Overestimations of the measurements may be a reason for such discrepancy.

- The total dry deposition of aerosol organic carbon is estimated to be 14 Tg C yr\(^{-1}\), the total aerosol wet deposition 78 Tg C yr\(^{-1}\). Both numbers are much higher than other global estimates, based on emission inventories. But in the same order of magnitude of estimated emission inventories. Again, important variability was noted in the estimated depositional fluxes of aerosol carbon.

- Dry aerosol carbon deposition can be significant in high latitude dust influenced regions where wind and aerosol mass enhance the dry deposition velocity. Also in ocean areas where sea-salt is dominant. However its magnitude is lower than other depositional mechanisms. Wet aerosol deposition is highly dependent on the precipitation rate, major in the ITCZ.

- Wet gaseous deposition is estimated to be 190 Tg C yr\(^{-1}\), but the validation of the methodology is not straightforward due to the uncertainties and variability when measuring DOC.

- Estimated diffusive fluxes of gaseous organic carbon show important figures, higher that our reported fluxes for dry and wet particle deposition of organic carbon, and already sizeable to the oceanic CO\(_2\) uptake. However the estimation lacks further experimental evidence. Research in this area is needed.

- The global spatially resolved models of POPs presented in previous chapters 3.2.3.2 - 3.2.3.6 present the following limitations, which should be accounted for future developments:
  - All water column particles behave like phytoplankton
  - Not considered role of microorganisms, colloidal phase, turbulent processes
  - Homogeneous concentration of POPs in the water column (well-mixed water column)
  - Assumed steady state
  - Not considered sediment processes, important in a more coastal environment
3.3 Water column POP dynamics

3.3.1 Rationale, background and outline of chapter 3.3.2

The developed 0-D model at steady state and spatially resolved was not adequate to investigate the short-term dynamics of POPs in a coastal or shallow aquatic environment. In that case it is necessary to account for the temporal variation of water concentrations, i.e. to use a dynamic model, and to account for sediment processes. Having this in mind, it was formulated the BIODEP model, applied to evaluate the atmosphere-water interactions in a high altitude lake. It is a 0-D dynamic model (level IV) where both atmospheric and sediment inputs are accounted, and constitutes as a first step to further formulate a 1D dynamic model. In the atmospheric part, the dry and wet deposition and diffusive air-water exchange are considered. Indeed, the modelling framework developed for the atmospheric deposition to the global oceans (chapter 3.2.3) was utile when implementing BIODEP. However, parameterizations of the BIODEP model were more empirically based than in 3.2.3 and accounted for other processes such as deposition by snow or the ice melting. Another novelty was the treatment of the water column as a one well-mixed compartment when no stratification occurs, but as two well-mixed compartments, i.e. epilimnion and hypolimnion when stratification takes place. Hence, turbulent mixing was assessed in a very simplified way, assuming that the contaminants are uniformly mixed in the hypolimnion or epilimnion, delimited by the depth of the thermocline. On the other hand, all water particles were assumed to behave like phytoplankton, as in 3.2.3, but the exchange of contaminants between water and particles was not described by equilibrium partitioning but by uptake and depuration kinetics with growth dilution taken into account. Further details are found in Meijer et al. (2006).

BIODEP model yielded results in agreement with experimental measurements within a factor of two. The role of sediments fluxes was proven important and, as happened in global estimations in this PhD-thesis and in other exercises in shallow aquatic environments (Baker et al., 1991; Blais et al., 2001; Ko et al., 2003; Palm et al., 2004). Furthermore, diffusive air-water exchange constituted a dominant mechanism controlling the dynamics of PCBs in the water column. However, the model was supported by the assumption of well-mixed compartments, i.e. one well-mixed compartment when no stratification occurs, and two well-mixed compartments, i.e. epilimnion and hypolimnion when stratification takes place, which could yield to inaccurate conclusions. In fact, it is uncertain that the turbulence can support the hypothesis of two well-mixed layers in stratification periods (Hornbuckle et al., 2004), even less of one well-mixed compartment the rest of the time. Additionally, different budget calculations have seen that only a small fraction of the particulate organic carbon produced in the surface, to which POPs tend to sorb, is exported to the bottom, due to the actuation of turbulent processes among others (Fasham, 2003). However, a detailed analysis of the role of turbulence on the fate of POPs is essentially non-existent as explained in 1.5.2.2. Its
complex parameterization, the scarcity of vertical profiles or time series of POPs or the assumption that vertical fluxes are driven by sinking fluxes of particle-bound compounds are reasons explaining this lack of a related comprehensive study.

The need of a close examination of the role of turbulent mixing in the dynamics of POPs and the need of analysing the vertical profiles and short-term variability of POPs were primary factors justifying the development of a 1-D dynamic coupled hydrodynamic-contaminant model to a continental shelf environment of 50 m depth in the northern Adriatic. The hydrodynamic sub-model is adapted from COHERENS and the contaminants sub-model is an improvement from the BIODEP model and considered the contaminant in 3 states: dissolved-colloidal-particulate. It was developed in collaboration with the Institute for Environmental and Sustainability in the Joint Research Centre in Ispra, where I did a 4-month stage. Its implementation is explained in chapter 3.3.2. This model was useful to evaluate the interplay of the different fluxes accounted in the atmosphere-water-sediments system. It should be noted again that this is the first time that the mutual effect between turbulent fluxes of POPs and the sinking of particle-bound compounds has been explicitly assessed. The following sketch presents the accounted contaminant processes:
The model accounted for the total suspended matter as two individual compartments because of its key role in the re-distribution of POPs in the marine environment (Baker et al., 1991; Swackhamer and Skoglund, 1991; Meijer et al., 2006). This novel approach allowed to distinguish between “physical” and “biological particles”, TSM$^{\text{phys}}$ and TSM$^{\text{biol}}$. In particular, TSM$^{\text{phys}}$ accounts for the atmospheric aerosol inputs and the resuspension of particles from the sediments, while TSM$^{\text{biol}}$ represents the total particulate of biological origin. Contaminants sorb differently to one or the other type of particles, since they are characterized by substantial different organic matter content (higher in TSM$^{\text{biol}}$). The related settling is also modelled differently: “physical” particles are characterized by the constant settling velocity ($w_s$); conversely, “biological” sinking, i.e. the fraction of primary production lost to sinking, is assumed to be proportional to the flux of organic matter collected in
the bottom (FOM) (Baines et al., 1994), as eq. 37:

\[ F_{\text{SINK}} = F_{\text{SINK}}^{\text{phys}} + F_{\text{SINK}}^{\text{biol}} \] [44]

“Physical” sinking flux in each layer: \( F_{\text{SINK}}^{\text{phys}} = W_{\text{se}} C_{\text{W}}^{\text{part,phys}} \)

“Biological” sinking flux in each layer: \( F_{\text{SINK}}^{\text{biol}} = C_{\text{W}}^{\text{part,biol}} F_{\text{OM}}^{\text{biol}} / \text{NZ}\times\text{TSM}^{\text{biol}} \)

where NZ is the total number of considered layers (50 in this case).

The 1-D dynamic model estimated surface enriched-depth depleted and benthic layer enriched vertical profiles of PCB concentrations with temporal resolution, in agreement with the few available measured values in pristine open-sea regions. The so-called turbulent layer was seen to delimit the extent to which atmospheric inputs diffuse to the water column. Within this layer, a significant short-term variability was encountered, highly dependent of precipitation pulses. It contrasted with more constant values close to sediments, in agreement with the higher capacity of sediments to retain POPs when compared to waters. Turbulence was also proven to explain the upward diffusion of pollutants coming from the sediments but its extent was seen to be compensated by the sinking of particle-bound compounds, acting as an opposing flux of similar magnitude.

This exercise has given the basis to further answer other important questions, such as what supports and controls the POP concentrations in the food web or to analyze in a further level of detail the interplay between atmospheric and sediments fluxes. Also the configuration of the model is open to further implications in 3D by a simple software switch or to the coupling with a complex ecological model. A first intriguing result (not shown in 3.3.2) was obtained when applying the developed model to a shallower water column, of 10 m depth. The resulting temporal variation of concentration profiles for PCB 180 is shown in Figure 24. The turbulent layer breaks and all the water column is well mixed. Sediments affect all the water column instead of only affecting the deeper 2-5 m as in the 50 m water column depth.