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3.2.2.3 Scientific contribution:

***The maximum reservoir capacity of soils for Persistent Organic Pollutants:
implications for global cycling***

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The maximum reservoir capacity of soils for persistent organic pollutants: implications for global cycling

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Major global terrestrial sinks/stores for POPs are identified and the significance of gradients between them discussed.

Abstract

The concept of maximum reservoir capacity (MRC), the ratio of the capacities of the surface soil and of the atmospheric mixed layer (AML) to hold chemical under equilibrium conditions, is applied to selected persistent organic pollutants (POPs) in the surface 'skin' (1 mm) of soils. MRC is calculated as a function of soil organic matter (SOM) content and temperature dependent K_{OA} and mapped globally for selected PCB congeners (PCB-28; -153; -180) and HCB, to identify regions with a higher tendency to retain POPs. It is shown to vary over many orders of magnitude, between compounds, locations and time (seasonally/diurnally). The MRC approach emphasises the very large capacity of soils as a storage compartment for POPs. The theoretical MRC concept is compared to reality and its implications for the global cycling of POPs are discussed. Sharp gradients in soil MRC can exist in mountainous areas and between the land and ocean. Exchanges between oceans and land masses via the atmosphere is likely to be an important driver to the global cycling of these compounds, and net ocean land transfers could occur in some areas.

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Keywords: POPs; Global cycling; Modelling

1. Introduction

The sources, environmental transport, fate and sinks of persistent organic pollutants (POPs) are increasingly seen as topics to be addressed at the global scale. International regulations and controls are in force to reduce the emissions of POPs into the environment (UNECE, 1998; UNEP, 1998), while regional and global emissions inventories and budgets provide information that will help predict future trends in ambient

levels, environmental distributions and residence times. The atmosphere is a critical compartment in the global transport and cycling of POPs. Atmospheric emissions and subsequent long-range atmospheric transport (LRAT) provide a mechanism to distribute POPs widely through the global environment. Soils are also critical to the global cycling of POPs, but for different reasons. Soil is a compartment with a large capacity for POPs and these chemicals have long half-lives in soils (Mackay, 2001). Some POPs, notably pesticides, have been deliberately applied to the soil, whilst cumulative atmospheric deposition has contaminated all soils with trace levels of these compounds (Meijer et al., 2003, 2002; Hassanin et al., 2004). In some situations soils are clearly a source of POPs to the atmosphere; Bidleman

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and co-workers have given several demonstrations of the significance of the supply of pesticides from soils to air on the regional scale, for example (Bidleman and Leone, 2004). Soils may therefore be a source of POPs to the atmosphere, or a storage compartment, or sink of atmospherically derived POPs. The balance between source and sink is complex, dependent on the compound, soil properties, environmental conditions, time, etc.

The deep oceans also act as a significant sink of POPs at the global scale (Dachs et al., 2002; Wania and Daly, 2002) while POPs remaining in the surface oceanic mixed layer (OML) can recycle back to the atmosphere by means of dynamic air–water coupling (Jaward et al., 2004a), thus contributing to their global dispersal and cycling. Indeed, POPs can exist in the atmosphere in the gas phase under ambient conditions. They may therefore re-cycle or ‘hop’ between environmental surfaces and the atmosphere. This could potentially occur repeatedly, so they may eventually reach environments far removed from the source region. The processes of global fractionation, enhanced deposition at low temperatures and ‘grass-hopping’, driven by atmospheric transport, have been hypothesized and investigated in several studies (e.g. Meijer et al., 2002, 2003; Wania and Mackay, 1996; Gouin et al., 2004). An assessment has not been performed, so far, for soils. The tendency for POPs to be re-emitted is a function of the chemical and the environmental conditions. For example, POPs have a high affinity for soil organic matter (SOM) and will be less readily emitted from a soil of high OM content and low temperature than from a low OM soil in a hot region. The surficial layers of soils and the OML are in contact with the atmosphere and undergo seasonal and shorter term temperature fluctuations. Surface soils also provide the interface to deeper soil layers, where POPs may be affected by various processes, such as transport to depth, degradation and occlusion into SOM. It is clear that the surficial soil layer is potentially very important to global POP cycling and fate. However, its ‘capacity’ to store POPs—relative to the atmosphere—may be highly variable spatially and seasonally as observed for surface oceans (Jurado et al., 2004).

The objectives of this paper were therefore: (a) to develop the MRC concept for the soil ‘skin layer’ and apply it to a range of POP compounds at the global scale and with season; (b) to illustrate differences and variability in surface soil MRC through case studies of soil/location scenarios and therefore identify those regions with higher tendencies to retain POPs; (c) to compare the theoretical MRC values derived in this paper with field data on PCBs and HCB in air and soils and to discuss the implications for global cycling; (d) to discuss areas where there are sharp gradients in MRC, and their significance; (e) to compare the relative MRC values of soils and surface oceans and discuss the

potential role of land–ocean interactions on the global cycling of POPs. Selected PCB congeners and HCB were investigated, to cover a range of physico-chemical properties and because global background soil field data are available for these compounds (Meijer et al., 2002, 2003).

2. Defining the MRC of the soil skin layer

The MRC is defined as the ratio of the inventories in the soil skin layer and the atmospheric mixed layer (AML) at equilibrium. Hence, the:

$$\text{MRC} = \frac{C_{\text{soil}} \times A \times d}{C_{\text{air}} \times A \times \text{AML}} \quad (1)$$

where C_{soil} and C_{air} are the concentrations in soil and air, respectively, A is the surface area (e.g. km²), AML is assumed to be 1000 m and d is the assumed thickness of the soil skin layer. A value for d of 1 mm was selected, to address the short-term or dynamic capacity of the soil skin to engage in air–surface exchange (Harner et al., 2001). An MRC of 1 means that a 1 mm soil skin layer contains the same amount of POP as a 1000 m column of air above it. MRC values > 1 indicate more chemical is partitioned to the soil than the air, while MRC values < 1 indicate that the overlying atmosphere contains more chemical than the underlying soil skin layer. Obviously assuming deeper soil layers increases the MRC. POPs certainly reach deeper soils but this study focuses on the surface skin, because of its role in soil–air exchange and thus active cycling of POPs.

The air and soil concentrations can be expressed in terms of fugacity, as the product of Zf , where Z is the fugacity capacity of the medium and f is the fugacity of the chemical (Mackay, 2001). Since MRC considers the theoretical maximum (i.e. equilibrium) reservoir capacity, by definition the fugacity in the two compartments will be equal. By assuming that a typical soil is made up of 60% solids, 20% water and 20% air:

$$\text{MRC} = \frac{0.6 \times Z_s + 0.2 \times Z_w + 0.2 \times Z_a}{Z_a} \times \frac{d}{\text{AML}} \quad (2)$$

where Z_s , Z_w and Z_a are the fugacity capacities of the solid, water and air fractions of the soil. Then, according to Mackay (2001):

$$Z_s = \frac{1}{RT} \quad \text{and} \quad Z_w = f_{\text{oc}} \times K_{\text{oc}} \times \rho \times Z_a \quad (3)$$

where R is the gas law constant, T is the absolute temperature, f_{oc} is the fraction of organic carbon in the soil, ρ is the soil density (kg/l). Z_w can also be expressed as:

$$Z_w = \frac{Z_a}{K_{\text{aw}}} \quad (4)$$

where K_{aw} is the dimensionless Henry's law constant. Therefore, as $K_{oc} = 0.41K_{ow}$ (Mackay, 2001):

$$Z_s = 0.41 \times f_{oc} \times K_{OA} \times Z_a \times \rho \quad (5)$$

where K_{OA} is the compound octanol-air partition coefficient and, given that the contribution of Z_a is negligible in the soil since dimensionless Henry's law constant are of the order of 10^{-2} or lower for PCBs:

$$MRC = \left[0.246 \times \rho \times f_{oc} \times K_{OA} + \frac{0.2RT}{H} \right] \times \frac{d}{AML} \quad (6)$$

K_{OA} is strongly temperature-dependent (Harner and Bidleman, 1996; Shocib and Harner, 2002) and spans several orders of magnitude in the range of ambient temperatures that occur globally. The soil MRC is directly proportional to the ratio of fugacity capacities of soil and air. This results in an expression (6) which is much simpler than that describing the MRC of the oceans, where the strong seasonal and spatial variability of dissolved and particulate phases need to be taken into account, together with the variable depth of the OML (Jurado et al., 2004).

3. The methodological approach

To apply Eq. (6) at the global scale, information was needed on the global distributions of temperature and SOM. Soil and ocean surface skin temperatures are available as monthly averages from remote sensing and with a spatial resolution of $1^\circ \times 1^\circ$. The temperature data used in the modelling exercise were obtained from the Climatology Interdisciplinary Data collection, NASA Goddard Space Flight Center DAAC (Along

Track Scanning Radiometer). SOM content was available (expressed as percent soil organic carbon (SOC)), extrapolated from over 4300 soil profiles characterized worldwide (Batjes, 2000), as an estimation of soil properties at a $0.5^\circ \times 0.5^\circ$ grid resolution (Fig. 1). The highest SOM values and extents occur in the northern hemisphere (NH), in northern Russia, Canada, Alaska and Scandinavia. The SOM values in the database used refer to the average of measurements in profiles taken to 30 cm. The SOM in the skin layer is therefore likely to be somewhat higher than this average, probably leading to an underestimation of the MRC values derived here.

4. Results and discussion

4.1. General comments and compound comparisons

MRC values ranged over more than five orders of magnitude, between compounds, locations and season, consistent with previous assessments indicating the variability of soil/compound sorption capacity (e.g. Hippelein and McLachlan, 1998). However, the regions with higher MRC values can now be identified at the global scale. Figs. 2–4 show the calculated MRCs for January and July, for PCB-28, -180 and HCB, respectively. Values were also calculated for PCB-153 and are discussed later. Lowest values (<0.1) were for HCB in July with soils of low SOM (e.g. the Sahara) (Fig. 4). Highest values (100,000 and more) were for PCB-180 in January for soils with high SOM (e.g. Siberia, Scandinavia, Canada and Alaska) (Fig. 3). The variability in MRC for a given compound is obviously just a function

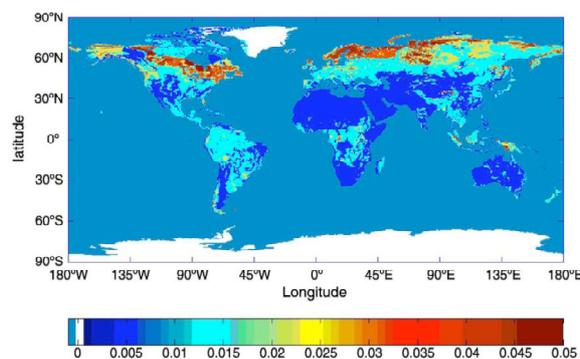


Fig. 1. The global distribution of soil organic carbon, expressed as a fraction (Batjes, 2000).

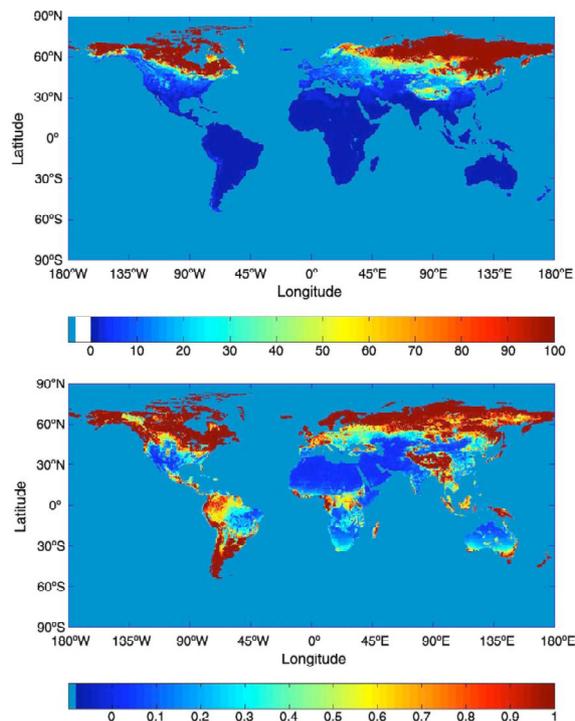


Fig. 2. MRC for PCB-28, January (A) and July (B). Different scales are used in the January and July MRC predictions.

of the variability in K_{OA} , induced by temperature, and in the SOM content. The former varies by around four orders of magnitude (e.g. $\log K_{OA}$ of PCB-28 varies from 1.9×10^{12} to 8.3×10^7 between -40 °C and 40 °C), while the latter varies by two orders of magnitude, between 0.1 and $>10\%$ SOC in the database used here (see Fig. 1). In addition to high latitude areas (such as Siberia), high mountain areas stand out as regions with higher potential for POP accumulation, consistent with previous observations (e.g. Ribes et al., 2003; Grimalt et al., 2004).

Two of the four compounds, PCB-153 and -180, always gave MRC values >1 , usually by three to four orders of magnitude. Indeed, they had MRC values ~ 10 – 100 , even for tropical locations in the summer. This emphasizes the very high capacity of soil,

relative to air, for these compounds. PCB-28 (Fig. 2) presents a rather different case from the heavier PCB congeners. In January most soils globally have MRC values >1 . However, in July, in many locations (notably equatorial Africa, much of Australia, eastern South America and the southern United States), the MRC values are <1 . HCB presents another contrasting situation. In January, most of the area above ~ 30 °N has MRC values >1 , with virtually all areas south of that being close to 1 or below it. In July almost all surface soils give values <1 for HCB.

4.2. Temporal variability

As noted in the previous section, there is marked seasonality in the MRC. This is emphasized further in

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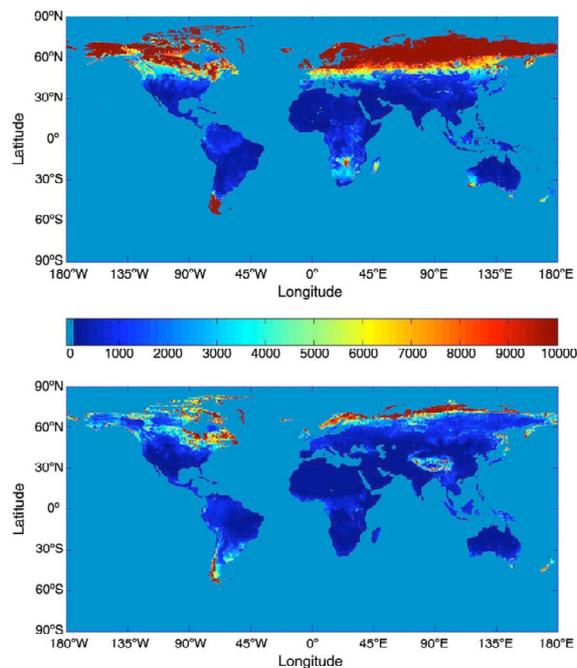


Fig. 3. MRC for PCB-180, January and July.

Fig. 5, where the ratio of MRCs for January and July for PCB-28 is plotted in some areas. The highest ratios (>100–1000) are observed in the same areas where the winter MRC is very high (i.e. Siberia, Canada and Alaska). Seasonal variability is also illustrated by considering some case study locations. Fig. 6 shows the MRCs of PCB-28 for selected locations in Siberia, Spain and the UK. At the Siberian site, a huge seasonal range in MRC is apparent, varying over three orders of magnitude. In contrast, the MRC only varies by a factor of 3–4 in the UK, where there is a moderate/maritime climatic. Temporal variability can also be important diurnally. The highest calculated diurnal variations were projected to occur in the North American Rocky Mountains, the Sahara, southern Africa and the Middle East, where they vary by about a factor of ten in January, for example. If the soil is supplying the atmosphere with a given POP, these MRC calculations show that

substantial changes in ambient air concentrations would be expected to occur seasonally and diurnally. It is instructive to compare these theoretical MRC calculations with field observations. Firstly, however, it is appropriate to acknowledge some of the assumptions and uncertainties behind the MRC approach.

4.3. Assumptions and uncertainties

4.3.1. SOM

Derivation of the MRC obviously relies on assumptions about the amount of SOM and its influence on compound partitioning. As noted earlier, the absolute amounts of SOM in surface soils may be underestimated by the database used here, having the net effect of underestimating calculated MRCs. All SOM is also assumed to have the same partitioning properties, regardless of whether it is peat, forest or grassland etc.

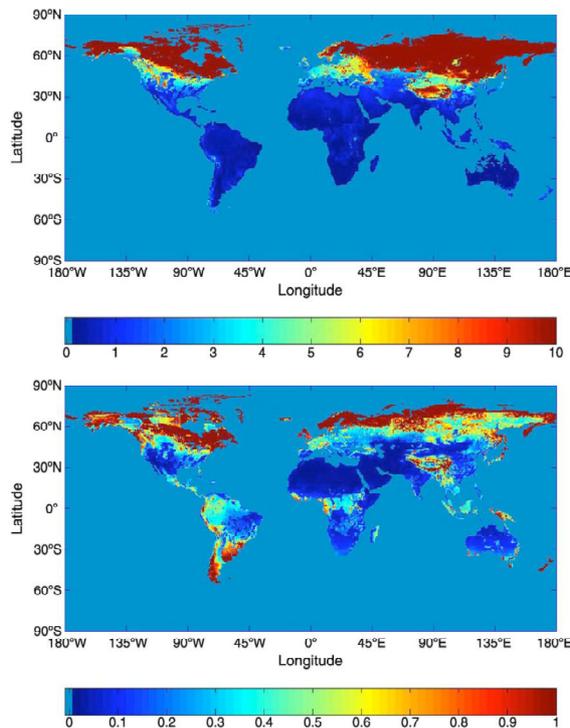


Fig. 4. MRC for HCB, January and July.

Seth et al. (1999) suggest that differences in SOM type may give rise to a variability of a factor of three or so, in modelled partitioning behaviour.

4.3.2. K_{OA}

Determination of K_{OA} is subject to experimental difficulties, and different values are reported for the same compound from different studies, thus introducing a degree of uncertainty (Mackay, 2001; Shoeb and Harner, 2002). Uncertainties are also introduced, because the measured temperature dependency of K_{OA} has to be extrapolated to the wider range of real world temperatures. This is most important at lower temperatures, because laboratory measurements have been made in the -10 to $+30$ °C range (Harner and Bidleman, 1996; Shoeb and Harner, 2002).

4.3.3. Low temperature conditions

Further uncertainties are introduced in the calculations made under lower temperatures, because soil physical properties change below freezing, and it is unclear what impact this has on compound partitioning behaviour. Fig. 6 provides an illustration of this point, by presenting two possible scenarios for the Siberian winter MRC values, one where the MRC has been calculated assuming the monthly average temperature measured by remote sensing, well below 0 °C (down to -50 °C) and the other where the temperature was assumed to be equal to 0 °C. The 'true' value for the MRC is likely to lie somewhere in this wide range.

It should be remembered that the MRC is a theoretical concept—it does not represent reality. This is particularly highlighted by the consideration of cold

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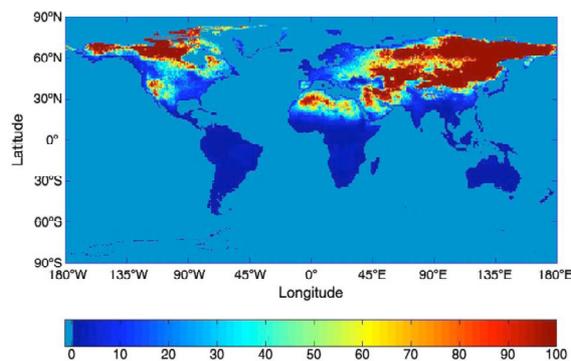


Fig. 5. Ratio of the January and July MRC values for PCB-28.

climates. There are many complicating and poorly understood factors which will affect air–soil exchange processes under field conditions. Air–soil gas exchange, leaching and bioturbation will all be negligible in frozen

soils, for example, while seasonal air–soil exchange will be strongly influenced by snow cover in many regions where the MRC is calculated to be at a maximum (i.e. Siberia, Canada, Alaska, Scandinavia).

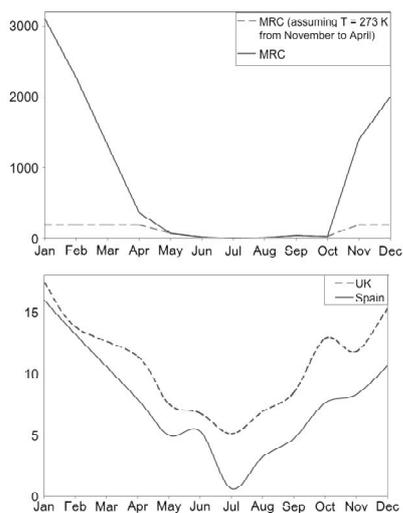


Fig. 6. Seasonal variabilities in MRC for PCB-28 at case study locations in Siberia, Spain and the UK.

4.3.4. Confounding factors influencing air–soil exchange

Snow has just been highlighted as one factor which may substantially deviate from the ‘model conditions’ considered by the MRC calculation, where air–soil partitioning is viewed purely in terms of gaseous exchange. In reality, of course, gas particle partitioning, dry particulate and wet deposition, and soil re-entrainment processes all occur and can be dominant for certain POPs in certain locations at certain times. Another major confounding factor is vegetation. It is in intimate contact with the atmosphere, moderates the soil temperature, micro-climate, and air–surface exchange, and—through cuticular shedding and leaf fall—provides additional air–soil transfer pathways for POPs under certain field conditions (see Barber et al., 2004).

4.4. Relating the theoretical MRC concept to reality

4.4.1. The storage capacity of soils for POPs

The soil MRC values highlight the very high capacity of soil, relative to air, for these compounds. This is emphasized by the fact that d is only 1 mm in the calculations performed here. Much of the land mass covered by high SOM soils in the NH, for example, can have many centimetres of soil humus (e.g. grasslands; deciduous and coniferous forests); indeed, it may extend down to many metres (i.e. in peat bogs), even though

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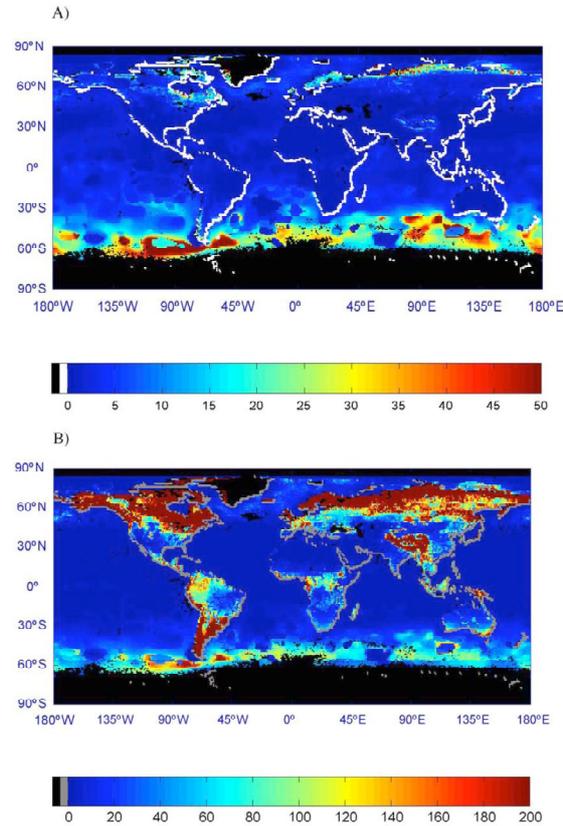


Fig. 7. Comparison between the soil and ocean MRC for (A) PCB28, (B) PCB153 for July. The black areas represent regions with no soil.

POPs in these deeper soils may not be available for soil–air exchange. Clearly these ecosystems have the propensity to act as major environmental repositories (sinks/stores) of POPs, *if* POPs ever reach these environments by LRAT *and* reach deeper layers following bioturbation, burial, downward transport, etc. A key question concerning the global fate and significance of POPs is therefore whether LRAT processes will supply significant amounts of POPs to those regions of the globe where soils of high storage capacity

are located, or whether the huge capacity of SOM-rich soils to store POPs will remain unrealized.

Supply of POPs to the soils of highest MRC (see Figs. 2–4) would require extensive LRAT, because the global source regions of industrial and agricultural chemicals are generally the temperate industrial latitudes of the NH (e.g. PCBs, PCDD/Fs, PBDEs), and the tropics (e.g. DDT). If POPs undergo repeated air–surface exchange, then ultimately they may ‘find’ (i.e. be deposited to) the soils of highest MRC. Alternatively,

they may be deposited to soils in or close to the source regions and—if those soils have sufficiently high MRC—be retained there instead. For example, a POP applied to soil or emitted to atmosphere in Africa or the southern US in the summer may readily move from that region because the soils there have a relatively low MRC. In contrast, a POP applied to soil or emitted to atmosphere in northern Europe in the winter, for example, may be retained locally because the soils there have much higher MRCs. In such locations, it then becomes important to consider whether the soils MRC for a given POP is reached—with the potential re-release of POP from the soil surface skin to atmosphere—or whether the soil MRC is so large that a net air–soil flux is maintained. Processes which mix the surface skin with deeper soil layers (e.g. bioturbation), ‘replenishing’ the SOM at the surface, would further maintain the soil’s capacity to act as a POP sink/store. In this context it is instructive to examine some field data and observations with respect to the MRC concept. This can be done by assessing whether the distribution of POPs between soil and air is approaching equilibrium, and by assessing the relationship between POP and SOM distribution, for example.

4.4.2. Assessment of PCB soil:air equilibrium status

Two PCB datasets where air and soil concentrations were measured concurrently at similar locations were evaluated. Both are in Europe, where the SOM (see Fig. 1) and background PCB values (Meijer et al., 2002, 2003) are relatively high. These were used to calculate soil:air fugacity ratios, to compare against the MRC values. An important assumption in these calculations is that the concentrations measured in the surface few centimetres of soil are representative of the surface 1 mm skin layer considered in the MRC calculations. It appears that very little information is available on POP distribution in finely resolved depth increments.

Meijer et al. (2002, 2003) determined a range of PCBs in 0–5 cm depth UK background soils, also reporting data on the SOM and soil density. Lee et al. (1998) and Lee and Jones (1999) have reported data for these compounds in UK background air. Table 1 presents the soil and air fugacities (Mackay, 2001) and the MRC at 10 °C. The soil:air fugacity ratio, expressed as a percentage of the projected equilibrium condition, was also derived. A fugacity ratio equal to 1 corresponds to equilibrium conditions, values <1 indicate a net air-to-soil transfer, whilst values >1 indicate the soil would supply the air. Different compounds obviously gave different values. All the PCBs had values considerably <1, with the lowest values for the heavier congeners (fugacity ratios of 0.01, 0.02 and 3×10^{-4} PCB-28, -153 and -180, respectively). Similar calculations were performed using experimental data recently obtained in southern Sweden by Backe et al. (2004). The Swedish study had higher soil concentrations and lower air concentrations than reported for the UK, which yielded fugacity ratios for the three PCB congeners that were about two orders of magnitude higher than those estimated for the UK samples. The Swedish results suggest that PCB-28 was near equilibrium, but—as for the UK study—net deposition of the heavier congeners. However, the higher temperatures present during summer may result in net volatilization.

4.4.3. Assessment of HCB soil:air equilibrium status

The same UK datasets (Meijer et al., 2002, 2003; Lee et al., 1998; Lee and Jones, 1999) were used to calculate the HCB soil:air equilibrium status for the UK (Table 1). On average, the fugacity ratio was close to, but slightly higher than 1, suggesting a condition of near equilibrium. This implies that, depending on the precise location and temperature, conditions of net deposition or volatilization may occur. HCB has a very homogeneous distribution in the atmosphere (Jaward et al.,

Table 1
MRC estimation and experimental data for the UK and Sweden

	MRC (at 10 °C)	Concentration in soil (ng/kg)	Soil fugacity (Pa)	Air fugacity (Pa)	Soil:air fugacity ratio (%)
UK (<i>n</i> = 30)					
PCB-28 ^a	44	100	1.2×10^{-11}	4.9×10^{-10}	1
PCB-153 ^a	900	700	3.9×10^{-12}	7.7×10^{-11}	2
PCB-180 ^a	5100	500	1.6×10^{-14}	2×10^{-11}	0.03
HCB ^a	2.0	550	2.1×10^{-9}	8.2×10^{-10}	103
Sweden (<i>n</i> = 11)					
PCB-28 ^b	75	145	2.4×10^{-11}	2.8×10^{-11}	86
PCB-153 ^b	700	3900	1.8×10^{-11}	2.8×10^{-11}	7
PCB-180 ^b	4000	3500	3.5×10^{-13}	1.1×10^{-11}	3
Global (<i>n</i> = 68)					
HCB ^a	6.7	629	7.3×10^{-10}	4.1×10^{-10}	180

^a Meijer et al. (2003); Lee et al. (1998).

^b Backe et al. (2004).

2004b). A global background air concentration of 50 pg/m³ was assumed, to assess the soil:air equilibrium status for this compound, coupled with the range of background soil concentrations reported previously (Meijer et al., 2003). On average the soil:air fugacity ratio was slightly >1 (ca. 1.8). However, broad differences were observed between background locations in the NH and more remote ones in the SH. In most locations in the NH, the fugacity ratio was somewhat >1, while in the more remote sampling stations in the SH it tended to be <1. HCB is probably the most variable and dynamic of the POPs.

In summary, these calculations suggest that the surface soil skin layer in background locations has still not reached its MRC for the high molecular weight congeners unless concentrations in the top millimetre are significantly higher than the average measured concentrations in the 0–5 cm range. Soil therefore continues to be, over the long term, a net sink for these PCBs emitted to atmosphere, despite the ongoing diffusive emissions of PCBs for many decades. The situation for lighter PCBs may be more complicated, with background soils acting as sources or sinks in different areas, at different times. It should be noted that the fugacity ratio is very sensitive to temperature, so that the favoured flux direction could shift daily or seasonally for a compound near equilibrium. These results are consistent with the observations that suggest that sorption to soil strongly retards global cycling of POPs (Meijer et al., 2002, 2003), due to the high capacity of soil to store POPs.

4.4.4. Observed seasonal and diurnal changes in air concentrations

It is clear from the earlier sections that the MRC varies seasonally and diurnally and that these changes can be substantial in some regions. For a compound close to air:soil equilibrium, these shifts would induce fluctuations in air concentrations, *if* (a) the kinetics are rapid enough, and (b) all other variables remain equal. In reality, of course, many other factors which influence ambient levels vary seasonally/diurnally: primary sources, the AML height, vegetation, deposition processes/rates, advection, etc. as has been discussed elsewhere (e.g. Lee et al., 1998). Studies on the diurnal trends of PCBs over land indicate rapid changes in air concentrations, correlated to ambient temperature, implying rapid kinetics of air-vegetation and/or air-soil exchange (Batjes, 2000; Hung et al., 2001). Day:night ratios for different congeners were typically 2–3:1, although under certain circumstances (Hornbuckle and Eisenreich, 1996) they can be as high as 10. Seasonal shifts in PCB air concentrations have been reported by various workers (e.g. Buehler and Hites, 2002). The observed variation in atmospheric concentrations in such studies is generally only a factor of 4–6 with summer > winter

(e.g. Lee and Jones, 1999; Halsall et al., 1999). As noted earlier, the seasonal variation in soil MRC can be much larger than this (e.g. see Fig. 5). These observations, taken together with the evidence of the previous section, imply that the seasonal variations in ambient PCB concentrations are probably controlled predominantly by factors other than air–soil exchange.

4.4.5. The relationship of POPs in soils with SOM and gradients in soil MRC

Some POPs have extremely long atmospheric characteristic travel distances (CTDs; Beyer et al., 2000) (e.g. HCB) so that, once airborne, they can travel great distances across the earth's surface. This may potentially be many thousands of kilometres, sufficient for them to pass over a very wide range of soils and a marked 'gradient' of soil MRCs. In fact, there is tremendous spatial variability in soil MRCs (Figs. 2–4). The net tendency of a chemical to travel may therefore be controlled by the compounds nearness to air:soil equilibrium. If the concentration of a given chemical in the surficial layer of the soil is much lower than its MRC it will tend to stick to the soil. If the soil has approached its MRC (i.e. in the lower SOM soils), then the compound will effectively have a greater travel distance. Clearly, on a global scale, there is the potential for great variability in compound behaviour. For example, a compound emitted in the southern US or southern Europe into a northerly moving air mass will pass over a very wide range of soils. Over a distance of some thousands of kilometres, it could potentially come into contact with very low (<1%) SOM contents in the south and very high (>10%) values in the north (see Fig. 1). Soils in the south are more likely to have approached their MRC for lower K_{OA} POPs, accentuating the compounds overall LRAT potential. Similar gradients in soil MRC occur over much shorter distances (kilometres to tens of kilometres), moving from floodplains, up valley sides to mountains. Temperature changes can be dramatic (decreasing on average by 1 °C every 200 m), whilst the % SOM can change markedly from quite high values in the low land areas and slopes to virtually 0% in areas scoured by seasonal snow cover. Despite this, air concentrations along such gradients appear to change rather little, suggestive of long CTD and net air–soil transfers.

HCB has a very high CTD, on account of its low atmospheric reactivity and low propensity to deposit (Beyer et al., 2000). However, its potential to travel long distances may be accentuated still further, because soils may have attained their MRC for this compound. In stark contrast, PCB-180 deposits to soils which have a much higher MRC for it. It is therefore retained close to the source. Proximity to source is therefore a major confounding factor in the relationship between soil POP concentration and SOM content (Meijer et al., 2003).

These processes will also contribute to the global fractionation of POPs, since heavier compounds may be retained close to emissions.

4.4.6. Soil versus ocean MRCs: a major driver to the global cycling of POPs

As just noted, gradients in surface MRC can exert an important influence on global POP cycling. It is instructive to compare the MRC values of soils and oceans (Dachs et al., 2002; Jurado et al., 2004), because these major surface compartments have different capacities for POPs. These vary with latitude and longitude and—as an air mass moves over a land/ocean boundary—a sharp transition in surface MRC can be experienced. To illustrate these features, Fig. 7 shows the soil and ocean MRC values for PCB-28 and PCB-153 for July. In most cases, the highest values are for soils, rather than oceans. During the NH winter, oceanic MRC values peak at $\sim 60^\circ\text{N}$, while soil values increase further northwards. In contrast, during the NH summer (July), the maximum oceanic MRC values tend to be in the SH, because of the large surface OML depth during winter (Dachs et al., 2002; Jurado et al., 2004). In the latter situation, SH oceanic MRC values can reach values higher than over land, a situation with implications for global cycling of POPs.

The land-ocean differences in MRC indicate that a given air mass will be exposed to very different surface reservoir capacities when moving from the ocean to the land, or vice versa. Particularly marked land-ocean MRC transitions occur for PCB-153 between the northern Pacific and western Canada, the southern Pacific/Atlantic and South America, and the eastern Atlantic and Europe, for example (Fig. 7). Consequently, POPs will tend to deposit to continental high latitude areas in the NH, but less so to the adjacent marine regions, especially, during times when settling rates of organic matter are low and thus water column POPs are not depleted in the OML (Dachs et al., 2002). Conversely, in the SH at the same time the southern ocean may act as a sink for those atmospheric POPs reaching that area. These differences in land-ocean capacities to retain POPs are clearly seasonally dependent, varying with oceanic phytoplankton biomass and OML depths (Dachs et al., 2002; Jurado et al., 2004). For tropical and equatorial regions, ocean and soil MRC values are similar and low in all cases, and thus land to ocean transfer of pollutants can be an important process. It has been suggested that gas phase concentrations are higher at low latitudes (Axelman and Gustafsson, 2002). In addition to higher temperatures, these regions are characterized by lower surface reservoir capacity (in both soils and oceans), encouraging LRAT.

Intriguingly, because there is often an ocean-land MRC gradient at high latitudes, net transfer of POPs from surface ocean waters, via air, to soils may occur. This is more marked during winter, when land temper-

atures are much lower than ocean temperatures and primary productivity and the associated removal due to settling particles is not efficient. This is at variance with the traditional view that activities on land are the source of marine pollution and that oceans are the 'ultimate global sink'. We speculate that the ocean would be a final sink during seasons with high productivity (spring and fall), when settling fluxes are enhanced and surface concentrations of POPs are much lower than those in equilibrium with the atmosphere (Dachs et al., 2002). Therefore, there is a strong seasonality in these ocean-land interactions that needs further research from both the experimental and theoretical approaches. Indeed, land ocean gradients are in some situations even higher than the ones observed for soil only or ocean only at different latitudes.

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3.2.2.4 Major issues and conclusions of chapters 3.2.2.2 and 3.2.2.3

- The “Maximum reservoir capacity” (MRC) of the surface oceans, i.e. the capacity of the surface oceans to store POPs relative to the atmosphere at equilibrium, gives indications of the tendency of compounds to be retained in surface water, delimited by the Mixed Layer Depth (MLD). It can be estimated only from biogeophysical parameters (chl a , SST, MLD) and POPs physico-chemical properties when considering a 0-D Level I model. Since it is independent of the actual occurrence of chemicals, the sensitivity to the different biogeophysical parameters is easily analyzed.
- The MRC in oceans is highly seasonal and variable spatially, affected significantly by phytoplankton patchiness. In the NH winter peaks of MRC are located around 60°N, not further north, indicative that the ratio is not governed solely by temperature, instead by phytoplankton biomass. Conversely, in the NH summer peaks are located around 60°S. However, those trends may also be affected by the mass of ice in the high latitudes, where the satellites used in the study fail to retrieve data.
- The temperature and physico-chemical properties aren’t enough to predict the reservoir capacity of the surface oceans, specially for the more hydrophobic PCBs and for high productivity regions. Indeed, biogeochemistry, specially interactions with biota play a critical role in the fate of PCBs and other POPs. Nevertheless those are not accounted by the Global Fractionation Theory, which should be complemented by these findings.
- Evidence of settling of POPs sorbed to organic matter as an important removal process from the surface ocean, outstanding in mid-high latitudes and upwelling areas and for the more hydrophobic compounds. This results in an enrichment of the surface ocean in the lower chlorinated PCBs, which are not effectively removed by the settling of biogenic particulate matter. It is also a prove of the importance of non-fugacity driven processes contributing to non-temperature driven fractionation of POPs at regional and global scales.
- Variability of the MRC soil surface skin layer is important; vegetation and snow may introduce important biases to the theoretical MRC ratio derived from equilibrium conditions. This affects the LRAT of POPs which will tend to be distributed towards the areas of highest MRC, highest soil organic matter. Again, this is not explained by the movement of POPs driven by temperature changes, following the Global Fractionation Theory.
- Comparison of the MRC values in the surface ocean with that in soils skin layer show an

important mass in soils, stressing the tendency of soils to retain POPs. Differences are more remarkable for the more hydrophobic PCBs, which are shown to be retained close to sources. Furthermore, sharp gradients between soil and ocean are observed in high latitudes.

- Gradients between soils and oceans MRC can exert an important influence on global POP cycling. Depleted ocean-land gradients in low latitudes and low MRC values both in soils and oceans in these latitudes favour the LRAT. Indeed land-to-ocean transfer of pollutants may be important in low latitudes, which could explain the high measured gas phase concentrations of POPs in these latitudes.

3.2.3 Deposition and sinks of POPs and organic matter for the global oceans

3.2.3.1 Rationale, background and outline of chapters 3.2.3.2 - 3.2.3.6

When examining the maximum reservoir capacity, as presented in the previous chapter, it was seen that the uptake of POPs by phytoplankton and the posterior settling by large particles played a major role in the occurrence of POPs in the surface waters. It was a further evidence that those sinking fluxes affected ocean-water exchanges of compounds, in agreement with previous observations and modelling exercises (Dachs et al., 1999; Larsson et al., 2000; Dachs et al., 2002b). Next, we questioned whether other non-fugacity driven processes such as deposition of atmospheric compounds could also affect significantly the occurrence and fate of POPs dynamics. Furthermore, since the variability of environmental parameters was determinant when evaluation the capacity of the surface oceans or soils to retain POPs, we predicted that atmospheric inputs may also be affected by this variability, which is an observation that has been already reported in numerous studies (see chapter 1.5.2.1). Indeed, we were interested in developing a spatially resolved global model that accounted also for the temporal variability of meteorological parameters. This was achieved using as inputs the monthly-mean satellite-derived data (see previous chapter of methodology 3.1 for more details), and calculating all the fluxes and other parameters of interest each month. It can be classified as a spatially resolved 0-D Level III model where both atmospheric deposition and sinking were accounted. The studied system is the surface ocean; inside POP concentrations are well mixed and at steady state:

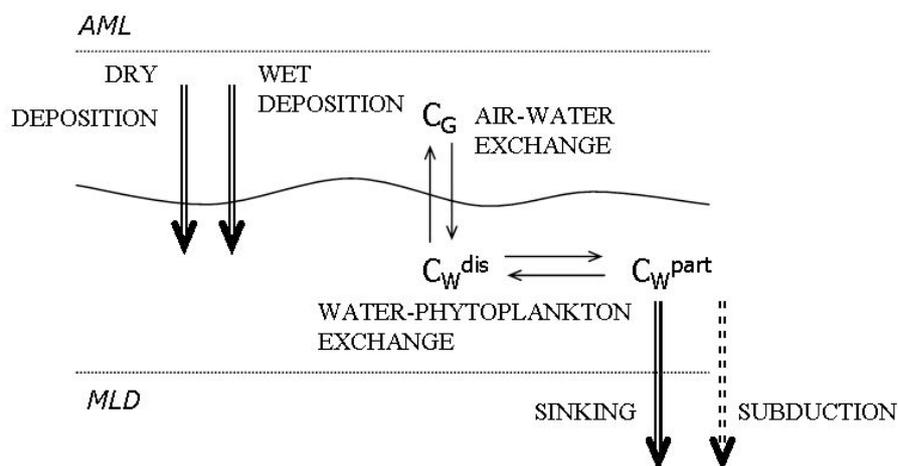


Figure 20 POP processes accounted in the 0-D steady state model

3.2.3.1.1 Atmospheric deposition fluxes of POPs and to the global oceans

The first purpose was to model and quantify the atmospheric depositional fluxes. Details of the methodology used is presented in chapters 3.2.3.2 and 3.2.3.3. In short, the model was applied each month to each “point” (pixel) of the Atlantic ocean using the monthly variation of the satellite data, physicochemical properties of the compounds and assuming constant in time measured atmospheric concentrations, which were assumed constant along the same latitude but varying for a certain longitude. Here it is shown (Figure 21) the latitudinal profiles of the measured concentration used as input data in the calculations (Lohmann et al., 2001; Jaward et al., 2004), which are not explicitly shown in the referred chapters 3.2.3.2 and 3.2.3.3 but can help in the interpretation of results and conclusions obtained:

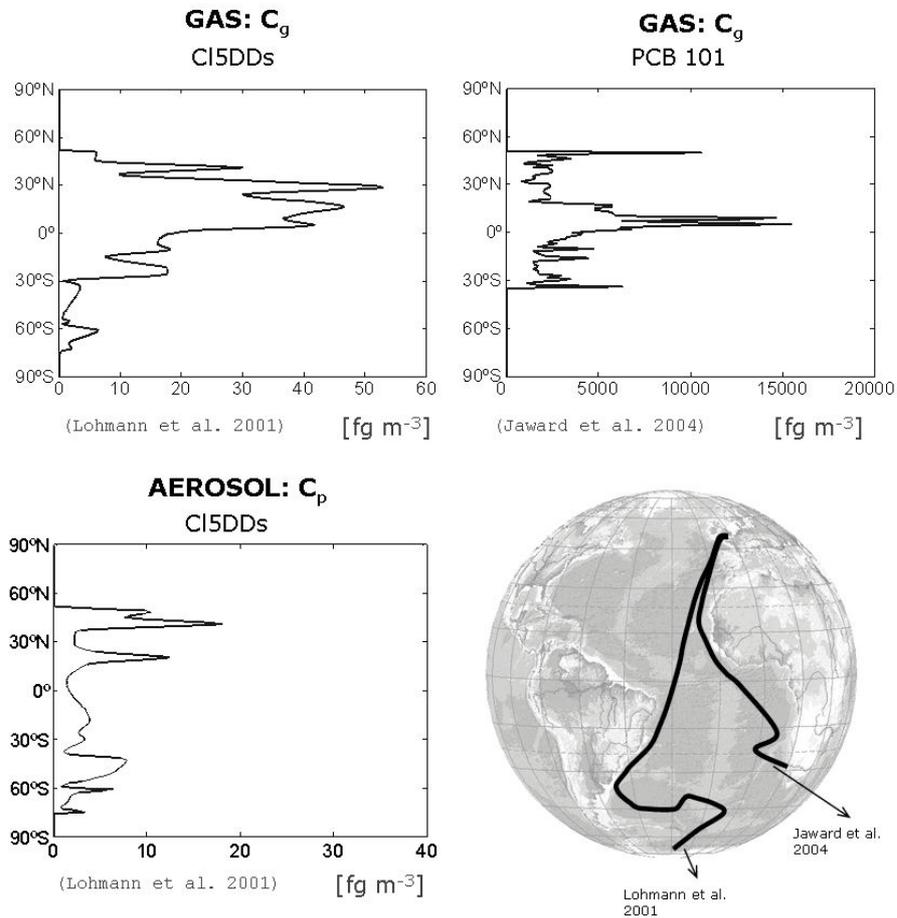


Figure 21 Profiles of the measured particle and gaseous phase POP concentrations used in 3.2.3.2 and 3.2.3.3

It is noteworthy the variability of the detected concentrations. Indeed, it is already foreseen the spatial variability in the transport fluxes of PCBs and PCDD/Fs, which justifies the use of a spatially resolved model. However, the variability of environmental variables such as wind speed, $\text{chl}a$, temperature, etc. can increase this variability. On the other hand, the particulate fraction presents increased values towards the poles, according to lower temperatures. Conversely, the gaseous fraction prevails in the low latitudes, where volatilization is significant. The latitudinal PCB profile also shows the influence of the contamination from urban centers at the beginning and at the end of the cruise.

Summarizing, the novelty of chapters 3.2.3.2 and 3.2.3.3 are: the use of satellite data to derive the transport fluxes of POPs, the estimation of a variable dry deposition velocity estimated at each point of the global oceans from wind speeds and sizes and amount of aerosols, the consideration of the rain in the calculations of the air-water exchange mass transfer coefficients and the consideration the adsorption of contaminants to the raindrops in addition to the diffusive absorption when evaluating the gaseous washout. In fact they represent improved parameterizations of the depositional fluxes presented in section 1.5.2.1, accounting for the available remote sensed data such as the variability of precipitation rates, wind speeds, chl *a*, temperatures aerosol sizes and mass, etc. Indeed we obtained a variability of depositional fluxes closer to the variability of biogeophysical parameters. The dependence of biogeophysical parameters has been overlooked in previous global modelling works, where the temperature was nearly the only driver or where properties didn't change along a given latitude (see chapter 1.3).. In short novel parameterizations are the following:

dry deposition: The overall dry deposition velocity was been obtained by averaging by weight the velocity of the midpoint fraction of each interval of sizes considered (it has been chosen 6 due to good results in different studies):

$$v_D = \sum_{i=1}^6 (v_{D,i} w_i) \quad [39]$$

The mass fraction of each of the intervals of sizes (w_i) were deduced from MODIS satellite parameters, relating the effective radius, which is deffined as the weighted integral of the volume-surface ratio, and its geometric standard deviation to the parameters of the lognormal distribution for the number concentration that usually characterizes the oceanic aerosols (see annexes in chapter 3.2.3.2). The velocity of the mid-point interval ($v_{D,i}$) was estimated by the Williams (1982) model that gives size and wind dependent dry deposition velocities.

Values obtained were comparable to those reported in previous studies of particle deposition velocities in coastal or lake environments (McVeety and Hites, 1988; Holsen et al., 1993), or modelling studies (Nho-Kim et al., 2004), which usually range from 0.1 to 0.8 cm s⁻¹. As noted earlier, MODIS characterization of aerosols fails to fully account for the importance of dust aerosols in desert outflow regions and therefore it is possible that v_D values are underestimated in some regions such as the Sahel-Saharan outflow over the Atlantic Ocean.

wet deposition: In the estimation of the gaseous washout it was considered both the absorption to the raindrop (W_{G_diss}) and the adsorption onto the surface of the raindrop (W_{G_ads}). It differs with the traditional parameterization of the gaseous washout, where only the absorption is considered (see 1.5.3.3 and 1.5.2.1.3). Practical consequences were that the variability of precipitation rate was also accounted in the gaseous removal of POPs by rain. This formulation has been used a posteriori by

other articles (Carafa et al., 2006).

air-water exchange: the air-water exchange flux during precipitation periods was distinguished from the one in dry periods. The air-water mass transfer coefficient during precipitation periods, was assumed as the additive result of the rain effect as suggested by Ho et al. (1997) and the wind effect as suggested by Nightingale et al. (2000a). They both result in an increase of the air-water mass transfer coefficient around a 10%, as suggested in chapters 3.2.3.2 and 3.2.3.3.

Details of the novel parameterizations of fluxes and results obtained are found in chapters 3.2.3.2 and 3.2.3.3.

Also we compared the dominant depositional mechanism for the global oceans. Equations for the gaseous absorption to the surface oceans and wet and dry deposition fluxes were arranged as the product of a mass transfer coefficient or velocity and the concentration of pollutant in one of the atmospheric phases. It can be understood as an analogy to a diagram of electrical resistances in parallel; each flux is associated to a resistance, or the inverse of a transfer coefficient. Then the dominant flux may be the one linked with the minor resistance or major mass transfer coefficient, independent of the aerosol- and gas- phase concentrations of the compounds. An approach with an analogy to electrical resistances has been also performed to obtain the equations that govern v_D or k_{AW} (Seinfeld and Pandis, 1998).

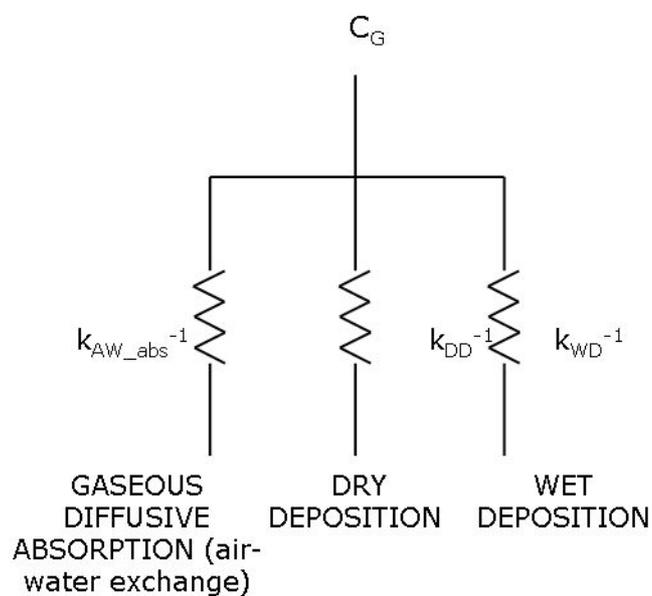


Figure 22 Analogy of POP fluxes between the atmosphere and the ocean to a diagram of electrical resistances (used in 3.2.3.2 and 3.2.3.3). k is the mass transfer coefficient.

3.2.3.1.2 Residence times over the global ocean atmospheres

Furthermore, residence times of POPs over the oceans were estimated from the spatially resolved atmospheric mass transfer coefficients or velocities from the deposition fluxes, using similar equations as the eq. 1. The novelty consist in the use of spatially resolved fluxes, a different approach that the one used in zonally averaged models or chemical transport models (see 1.4). First implications and results are shown in chapter 3.2.3.4.

3.2.3.1.3 Subduction fluxes as a sink of POPs

Taking into consideration the importance of deep water formation in some oceanic regions, we asked ourselves if this convection of surface waters to deep ocean could carry significant amounts of POPs. This was also suggested by the high MRC values in the regions were there is formation of deep oceanic water. It resulted in an article presented in chapter 3.2.3.5, pioneering in the subject.

Deep water formation regions are namely the Norwegian and Labrador Seas in the North Atlantic and the Weddell and Ross Seas in the Southern Ocean (Rahmstorf, 2002). Subduction fluxes (F_{subd} [$\text{kg m}^{-2} \text{y}^{-1}$]) were estimated at each region and assumed negligible at the rest of the oceans. They were parameterized as the product of the water concentration of the compound (dissolved+particulate) and the rate of deep water formation of the chosen area (r_{subd} [Sv]), divided by the area of interest (A [m^2]), where $3.15 \cdot 10^{-5}$ is a conversion factor

$$F_{\text{subd}} = \frac{C_{\text{W}}^{\text{tot}} r_{\text{subd}}}{A} 3.15 \cdot 10^{-5} \quad [40]$$

The magnitude of each flux was compared to the sinking of particle-bound contaminants, parameterized as described in Dachs et al. (1999; 2002b) and chapter 3.2.3.2. In particular, they are the product of the PCB concentration in the particulate organic matter phase, obtained from the dissolved phase using bioconcentration factors, and the vertical flux of organic matters as given by Baines and Pace (1994) from chl *a* satellite measurements.

Again meteorological satellite derived parameters were used for such estimations. But for the concentrations of POPs, regional measurements were accounted (Schulz-Bull et al., 1998; Sobek and Gustafsson, 2004; Gambaro et al., 2005).

3.2.3.1.4 Atmospheric deposition of organic carbon to the global oceans

As was stressed in the Introduction section, POPs are not only tracers for the total organic carbon but since they are hydrophobic, their dynamics are related. Therefore we adapted and performed the methodology to estimate global atmospheric deposition of POPs, which gave a good agreement between modelled and measured fluxes, to estimate the atmospheric deposition of organic carbon to the global oceans (see chapter 3.2.3.6). Results are important since it is the first comprehensive estimation of the global dry, wet deposition and diffusive air-water exchange of total organic carbon and numbers may contribute significantly in the budget of the marine carbon cycle.

Dry and wet deposition of aerosol organic carbon were computed from a size-dependent dry deposition velocity, a constant value of $W_{\text{p}}=2 \cdot 10^5$ as done for POPs (3.2.3.2, 3.2.3.3) and organic and black carbon concentrations as determined from dominant plumes of aerosols from optical values (see Figure 15, and supplementary material in 3.2.3.6). This determination of particle-concentration of organic and black carbon resulted in surprising good correlations between measured and modelled values, despite the simplicity, but also the originality of the method. Furthermore, the potential importance and probable magnitude of gaseous wet deposition and diffusive exchanges of organic carbon were discussed. However, we encountered difficulties to use

experimental data since the air-water exchange of total organic carbon is largely unexplored besides a recent study from Dachs et al. (2005), who suggested that on a regional basis diffusive air-water exchange of total organic carbon may be very important.

In short, the estimated fluxes of deposition of organic carbon were based on the following developed parameterizations:

dry deposition

$$F_{DD_OC} = v_D C_{P_OC} \quad [41]$$

wet deposition

$$F_{WD} = p_0 W_P C_{P_OC} + (p_0 / H') C_{GOC} \quad [42]$$

air-water exchange

$$F_{AW_OC} = k_{AW} \left(C_{EDOC} - \frac{C_{GOC}}{H'} \right) \quad [43]$$

where C_{GOC} and C_{EDOC} are the gaseous and dissolved organic carbon concentrations. C_{GOC}/H' is assumed $40 \mu\text{M}$ and $(C_{EDOC} - C_{GOC}/H') = 1 \mu\text{M}$ (Willey et al., 2000; Dachs et al., 2005). Further details are found in 3.2.3.6

3.2.3.2 Scientific contribution:

Atmospheric dry deposition of persistent organic pollutants to the Atlantic ocean and inferences for the global oceans

Jurado, E., Jaward, F., Lohmann, R., Jones, K. C., Simó, R., Dachs, J.
Environmental Science & Technology. 38 (21), 5505-5513

Jurado, E.: modelling, interpretation and writing

Jaward, F.: measurements of PCBs in oceanic air

Lohmann, R.: measurements of PCDD/Fs in oceanic air and interpretation

Jones, K. C.: interpretation

Simó, R.: interpretation

Dachs, J.: support with interpretation and writing

Atmospheric Dry Deposition of Persistent Organic Pollutants to the Atlantic and Inferences for the Global Oceans

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Atmospheric deposition to the oceans is a key process affecting the global dynamics and sinks of persistent organic pollutants (POPs). A new methodology that combines aerosol remote sensing measurements with measured POP aerosol phase concentrations is presented to derive dry particulate depositional fluxes of POPs to the oceans. These fluxes are compared with those due to diffusive air–water exchange. For all polychlorinated biphenyl (PCB) congeners and lower chlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs), air–water exchange dominates the dry deposition mechanism. However, this tendency reverses in some areas, such as in marine aerosol influenced areas and dust outflow regions, consistent with the important variability encountered for the depositional fluxes. Seasonal variability is mainly found in mid-high latitudes, due to the important influence of wind speed enhancing dry deposition fluxes and temperature as a driver of the gas–particle partitioning of POPs. The average dry aerosol deposition flux of Σ PCBs and Σ PCDD/Fs to the Atlantic Ocean is calculated to be in the order of $66 \text{ ng m}^{-2} \text{ yr}^{-1}$ and $9 \text{ ng m}^{-2} \text{ yr}^{-1}$ respectively. The total dry aerosol deposition of Σ PCBs and Σ PCDD/Fs to the Atlantic Ocean is estimated to be 2200 kg yr^{-1} and 500 kg yr^{-1} , respectively, while the net air–water exchange is higher, $22000 \text{ kg } \Sigma$ PCBs yr^{-1} for PCBs and $1300 \text{ kg } \Sigma$ PCDD/Fs yr^{-1} . Furthermore, it is suggested that marine aerosol plays an important role in scavenging atmospheric contaminants.

Introduction

After being emitted or revolatilized, persistent organic pollutants (POPs) partition between the gas and aerosol phases and are subject to long-range atmospheric transport (LRAT). Semivolatile organic compounds may then be removed from the atmosphere to the ocean by three main processes: dry deposition of particulate-bound pollutants, diffusive gas exchange between the atmospheric boundary

layer (ABL) and the surface ocean, and scavenging by rain (either from gas or particulate phases). Atmospheric depositional processes play a key role in the transport and fate of POPs at the regional and global scale (1–8). Furthermore, dry aerosol and gaseous deposition contribute to aquatic ecosystems pollutant burden and support POP accumulation in aquatic food webs (9, 10). Previous reports comparing the different removal mechanisms show that diffusive air–water exchange dominates over wet and dry particle deposition for POPs predominantly found in the gas phase, except in rainy regions and close to urban areas with high concentration of atmospheric particulate matter. Conversely, dry particle deposition is important for chemicals that have a strong affinity to aerosols such as polycyclic aromatic hydrocarbons (PAHs) (11).

Generally, reported measurements of POP atmospheric deposition refer to local ground-based measurements. There are very few studies dealing with remote and pristine oceanic regions (12), even in the remote areas characterized by elevated concentrations of aerosol, such as the Saharan dust outflow over the eastern Atlantic Ocean. Considering the lifetime of aerosol distributions and the important temporal and spatial variability associated to deposition and air–water exchange, it is clear that simple extrapolations to derive large scale estimations of both fluxes from these local measurements could introduce an important bias in the estimation. In this context, satellite retrieval data of aerosol characteristics provides valuable information that allows a synoptical view of biogeophysical variables and can be used to estimate deposition at the regional and global scale. The first aerosol data from remote sensing were obtained in the mid-1970s. Important technical improvements have been made since then, triggered by studies of the influence of aerosols on climate change. Recent advances in space-borne instruments allow derivation of not only the aerosol concentrations but also parameters characterizing their size distributions (13). It is therefore now possible to assess the spatial and temporal variability and significance of dry aerosol deposition and air–water exchange of POPs at the global scale.

In short, the goals of this study are to (i) use remote sensing data from sensors designed to monitor aerosol distributions to predict dry deposition velocities of aerosols and aerosol-bound POPs at the global scale; (ii) develop a methodology to estimate the spatial and temporal variability of dry deposition of POPs for the Atlantic Ocean, derived from atmospheric measurements of gas- and aerosol-phase POP and from satellite data; and (iii) assess the relative importance of dry particle deposition and air–water exchange for the Atlantic Ocean and at the global scale. It is believed that the techniques developed here and their applications can contribute to an improved understanding of atmospheric depositional processes at the regional and global scale, an issue of increasing concern (14, 15), and to help predict future trends of global POP fate under different climatic scenarios.

Field Measurements and Data Sources

Cruise Data. This work is based on atmospheric ship-board air concentrations of two representative families of POPs: polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) and polychlorinated biphenyls (PCBs). Data were obtained during two north–south Atlantic Ocean transects. PCDD/Fs were measured in air sampled on board the *RRS Bransfield* during an Atlantic cruise from the U.K. to Antarctica in October–December 1998 (52° N, 1° E–75° S, 20° W) (16). The PCB data were collected between The Netherlands and South Africa in January–February 2001 on board the *RV*

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Pelagia (52° N, 1° E – 34° S, 20° E) (17). Gas- and aerosol-phase POP concentrations were obtained from high volume samplers. In the case of PCBs, only gas-phase concentrations were determined, since PCB concentrations in the aerosol phase were below the detection limit. Latitudinal profiles of PCDD/Fs showed variability, with higher gas-phase values at low latitudes than at mid-high latitudes. PCBs present were detected throughout the cruise; the highest gas-phase detected values were found around 10° N and for samples where the air mass came from land. Both compounds displayed a gradient with concentrations decreasing from the northern hemisphere (NH) to the southern hemisphere (SH). Details of the methods, data variability, and trends are given elsewhere (16, 17) and in the Supporting Information (Annex I).

Satellite Data. Meteorological Variables: Sea Surface Temperature and Wind Speed. Sea surface temperatures (SST) were obtained from the Along Track Scanning Radiometer (ATSR) on the European Space Agency ERS-2 satellite (ATSR project Web page <http://www.atsr.rl.ac.uk>). SST images consist of monthly averaged skin layer temperatures with a resolution of a half degree and an accuracy of ± 0.3 K. Temperatures in the air film layer adjacent to the sea surface have been assumed the same as SST. Monthly global wind speed distributions were obtained from the NOAA special sensor microwave/imager (SSM/I) at a resolution of $1^\circ \times 1^\circ$ and an accuracy ± 2 m s⁻¹ (<http://lwl.ncdc.noaa.gov/oa/satellite/ssmi>). There is a lack of these estimations in latitudes close to the poles, depending on the ice coverage. The data used correspond to monthly mean values for the period of field sampling—November 1998 or January 2001.

Aerosol Data. Aerosol parameters were obtained from the Moderate-Resolution Imaging Spectrometer Instrument (MODIS, <http://modis.gsfc.nasa.gov/>) on board the Terra satellite, part of NASA's Earth Observing System (EOS). Since MODIS remote sensing parameters for aerosol data were not available before mid 2001, climatological means for November and January of two consecutive years (2002, 2003) were used. Monthly climatological means of level 3 aerosol products such as the effective radius (r_{eff} , μm), its standard deviation ($\log(\sigma_{\text{eff}})$, $\log(\mu\text{m})$), the aerosol optical depth (AOD), and the fine (submicron size) mode fraction (η) have been used (http://lwl.ncdc.noaa.gov/data/atlas4/MODIS/02_Atmosphere/02_Level_3). The advantage of MODIS retrieved data over other sensors is the information on aerosol size parameters. MODIS measurements of r_{eff} , $\log(\sigma_{\text{eff}})$, η , and AOD are integrated over the air column, for the aerosol size range detected by the instrument (aerosol diameters from 0.1 to 20 μm) and with a resolution of $1^\circ \times 1^\circ$. They have an approximate accuracy of ± 0.1 μm for r_{eff} , 25% for η , and $\pm 0.03 \pm 0.05$ AOD for the AOD (18). Uncertainty is higher in regions with possible cloud contamination, over ice cover and over coastal areas and marshes. In dust regimes retrieved size parameters (r_{eff} , $\log(\sigma_{\text{eff}})$) can underestimate up to about 40% (19, 20) of the actual aerosol size.

Model Development

Dry Aerosol Deposition Flux. Experimental measures of dry aerosol deposition fluxes (F_{DD} , $\mu\text{g m}^{-2} \text{d}^{-1}$) are scarce and fluxes are often estimated by

$$F_{\text{DD}} = v_D \times C_p \quad (1)$$

where v_D is the overall aerosol dry deposition velocity (m d^{-1}) and C_p is the POP aerosol-phase concentration ($\mu\text{g m}^{-3}$) (4, 21). v_D values are strongly dependent on aerosol size distribution, atmospheric turbulence (as influenced by wind speed), and at low wind speed by atmospheric stability. Pioneering studies that parametrized dry deposition velocities over natural surface waters, such as the models of Williams

(22) and Slinn and Slinn (23), still provide useful and widely used synopses for estimating v_D values (24–26). This study has been based on the widely used Williams parametrization (22), which determines v_D values as a function of aerosol diameter, wind speed, and atmospheric stability. Additionally, it includes effects of spray formation under high wind speed conditions and particle growth due to high relative humidities. Previous studies have shown that dry deposition flux estimations from a distribution of aerosol size derived v_D values are more accurate than using a single overall v_D value (29, 30). Therefore, assuming the aerosol size distribution is known, the aerosol diameter range is divided into a number of intervals (i), so that the total flux is given by

$$F_{\text{DD}} = \sum_i (v_{D,i} \times C_{p,i}) \quad (2)$$

where $v_{D,i}$ (m d^{-1}) is the deposition velocity for an atmospheric particle with a diameter in the midpoint of the interval i and $C_{p,i}$ ($\mu\text{g m}^{-3}$) is the corresponding POP concentration in the particle phase.

Aerosol size distribution over the oceans can be determined from the remote sensing measurements of aerosol r_{eff} , which is defined as the weighted integral of the volume-to-surface ratio, and $\log(\sigma_{\text{eff}})$ mentioned above. Assuming the size distribution is log-normally distributed, which is a common assumption for remote homogeneous aerosols (18, 31, 32), r_{eff} and $\log(\sigma_{\text{eff}})$ can be related to the median radius (r_g , μm) and the geometric standard deviation ($\log(\sigma_{\text{rg}})$, $\log(\mu\text{m})$) (33) by

$$r_{\text{eff}} = r_g \exp\left(\frac{5 \log^2(\sigma_{\text{rg}})}{2}\right) \quad (3)$$

$$\log^2(\sigma_{\text{eff}}) = \exp(\log^2(\sigma_{\text{rg}})) - 1 \quad (4)$$

Once the parameters r_g and $\log(\sigma_{\text{rg}})$ are determined, the mass fraction of aerosols of size midpoint i (w_i , dimensionless) to total suspended particulate matter values (TSP, kg m^{-3}) can be derived as described in Annex II (Supporting Information). In this study, 6 intervals of aerosol diameters have been considered among the range available from MODIS on the Terra satellite ($D_{\text{min}}-D_{\text{max}}$ (μm): 0.1–0.6, 0.6–1, 1–2, 2–3, 3–5, 5–20). Figure 1 shows TSP and two characteristic distributions of w_i for the Atlantic Ocean. The distribution of size fractions suggests that most of the aerosol mass is predominantly accounted for aerosols with diameters between 1 and 2 μm , even though the highest number of concentrations occur in the range 0.1–1 μm . The former range of sizes accounts for an important part of the plume resulting from dust in the Saharan desert (20–25° N) and from the Sahel region (10–15° N) of northern Africa, flowing across the Atlantic toward the Sargasso and the Caribbean Seas. Increased loadings of submicron aerosols are found during some months, close to industrialized countries in the northern Atlantic and in smoke biomass burning areas such as west-central Africa. Interestingly, submicron particles and aerosols in the range 1–3 μm are found over the southern mid-latitudes, which can be attributed to marine aerosol, i.e., salt particles emitted from bursting sea foam during windy conditions.

POP distribution to aerosols of different sizes needs to be accounted, but different studies give different size distribution information, and no assessment exists for the oceanic atmosphere (34). For example, some authors suggest higher POP concentrations in submicron aerosols (35, 36), while others find different aerosol size distributions of POPs (37–40). Therefore, POP concentration has been assumed to be uniform over the size spectrum of aerosols. The influence of this assumption is discussed below.

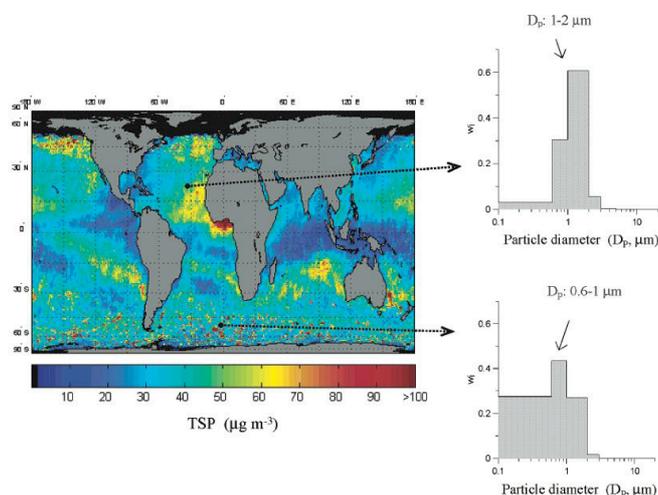


FIGURE 1. Aerosol concentrations over the surface ocean (TSP , $\mu\text{g m}^{-3}$) derived from the aerosol optical depth given by MODIS. Values from climatological January 2002–2003. Aerosol size distribution (w) are shown for characteristic oceanic regions (in Peters Projection of the world: equal area presentation).

Therefore, the POP concentration in aerosol size i ($C_{p,i}$) is proportional to the mass fraction of particles in the interval (w_i , see Annex II) and F_{DD} is given by

$$F_{\text{DD}} = \sum_{i=1}^6 (v_{\text{D},i} \times w_i \times C_p) = C_p \times \sum_{i=1}^6 (v_{\text{D},i} \times w_i) \quad (5)$$

and the overall mass averaged dry deposition velocity (v_{D}) is given by

$$v_{\text{D}} = \frac{\sum_{i=1}^6 (v_{\text{D},i} \times w_i)}{\sum_{i=1}^6 w_i} \quad (6)$$

Estimates of v_{D} are parametrized as described by Williams (22), and therefore $v_{\text{D},i}$ values for the different aerosol sizes i can be determined. These $v_{\text{D},i}$ values show a strong dependence on wind speed, especially for small aerosols ($<1 \mu\text{m}$) where turbulent diffusion becomes a dominant mechanism. Wind speed has a nonlinear influence on dry deposition. Monthly averaged wind speeds have therefore been corrected by taking into account the Weibull distribution of wind speeds over oceanic regions (41). The resulting dry deposition velocities ($v_{\text{D},i}$) are increased 20%, on average, due to nonlinear influence of wind speed, but this effect is very sensitive to aerosol size. Methodological details of the derivation of $v_{\text{D},i}$ are given in Annex III (see Supporting Information).

Figure 2 presents a global map of the overall dry deposition velocity over the oceans, in January 2002–2003. It shows significant spatial variability, where raised values are related to either high wind speeds (such as in mid-high latitudes of the northern and southern hemispheres) or larger fractions of mass concentration of coarse aerosols ($>1 \mu\text{m}$). v_{D} values range from 0.01 cm s^{-1} to 0.8 cm s^{-1} . These values are

comparable to those reported in previous studies of particle deposition velocities in coastal or lake environments (21, 42), or modeling studies (26), which usually range from 0.1 to 0.8 cm s^{-1} . However, a notorious spatial variability of v_{D} values occurs. As noted earlier, MODIS characterization of aerosols fails to fully account for the importance of dust aerosols in desert outflow regions, and therefore it is possible that v_{D} values are underestimated in some regions such as the Sahel-Saharan outflow over the Atlantic Ocean.

Predicted Gas-Particle Partitioning of PCBs. For PCDD/Fs, both gas- and aerosol-phase concentrations for the Atlantic Ocean transect were measured (16). However, in the case of PCBs, it was necessary to infer the particle-phase concentration from the measured gas-phase concentration, since it was not measured during the 2001 sampling campaign as described above. This can be done by (43)

$$C_p = C_g \times \text{TSP} \times K_p \quad (7)$$

where C_g is the gas-phase concentration (pg m^{-3}), and K_p ($\text{m}^3 \text{ kg}^{-1}$) is the particle-gas partition coefficient. The atmospheric columnar aerosol concentration (kg m^{-2}) can be derived from the aerosol optical depth (AOD), the fine mode fraction (η) and τ_{eff} through a recent algorithm developed by Gassó and Hegg (44). The mass concentration at sea level, or total suspended particle matter (TSP, kg m^{-3}), is obtained, assuming a relative humidity correction to the remotely sensed data, the same used to parametrize v_{D} (Annex III) and assuming that the aerosol is located and distributed homogeneously in the ABL (first 1000 m of air over the ocean). This last assumption results from the fact that satellite measurements are air-column integrated, and the variability of the vertical profiles of aerosols, which have a layered structure (45). However, the above assumption is consistent with the tendency of aerosols in the ABL over open oceans

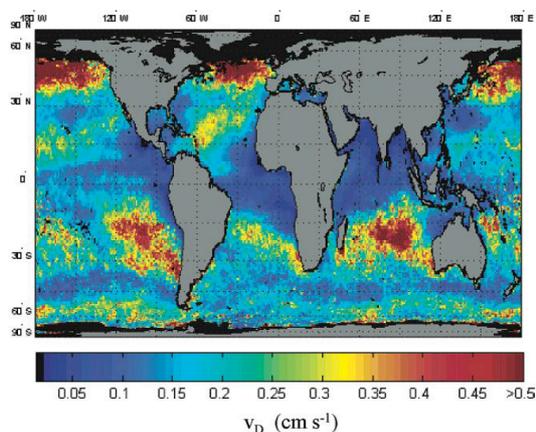


FIGURE 2. Map of overall dry deposition velocity (v_D) for the global Oceans. Values are referred to January 2001.

to be homogeneously mixed (31). Oceanic TSP values for November 2002–2003 are shown in Figure 1. Higher aerosol mass concentrations are found in the mid-high latitudes of the SH and in the dust outflow regions. Lower values are located along the Intertropical Convergence Zone (ITCZ), presumably due to the important role of precipitation scavenging in this region.

POP partitioning to aerosols has been described using two different sorption mechanisms: absorption into the organic phase of aerosols and adsorption onto soot carbon, as described elsewhere (46–49). The former has been successfully employed to model aerosol–gas partitioning of a wide range of POPs, such as PCBs and polychlorinated naphthalenes (PCNs), using the octanol–air partition coefficient (K_{OA} , dimensionless) as a predictor of the gas–organic matter partitioning. Due to the difficulty in determining the fraction of aerosol organic carbon from remote sensing measurements, a value of 15% has been considered representative over the oceans, consistent with measurements in open ocean (12, 50). In the present paper, K_P values determined experimentally for PCDD/Fs have been used, except in the seasonal trends section for the January, April, and July estimations. For example, K_P values ranged between 2×10^{-3} and 2×10^{-1} for Cl₂DD and between 2×10^{-2} and 4×10^{-1} for OCDD. Adsorption onto the soot fraction of atmospheric aerosols may be an important mechanism affecting the gas–phase partitioning of PCDD/Fs, as has been observed for PAHs (49), but not so important for most PCBs. In this case, the K_P is driven not only by absorption into the organic matter (K_{OA}) but also to adsorption onto the soot phase (soot/air partition coefficient K_{SA} , $m^3 kg^{-1}$), with elemental carbon being a surrogate for soot. It has been assumed a ratio OC/EC of 5, in agreement with measures in marine and remote areas (31, 34).

Gas Absorption and Net Air–Water Exchange Fluxes. Net diffusive gas-exchange (or dry gaseous deposition) is driven by the concentration gradient across the air–sea interface and depends strongly on wind speed, temperature, and compound specific physical–chemical properties, which all influence the mass transfer coefficient (k_{AW} , $m d^{-1}$). Absorption ($F_{AW,abs}$, $pg m^{-2} d^{-1}$) and volatilization fluxes

($F_{AW,vol}$, $pg m^{-2} d^{-1}$) are computed respectively by

$$F_{AW,abs} = k_{AW} \frac{C_G}{H'} \quad (8)$$

$$F_{AW,vol} = k_{AW} C_W \quad (9)$$

where C_W is the POP dissolved-phase concentration ($pg m^{-3}$) and H' (dimensionless) is the temperature and salinity corrected Henry's law constant. The net air–water exchange flux (F_{AW} , $pg m^{-2} d^{-1}$) is given by the difference of absorption and volatilization fluxes. C_W values have been obtained by applying a model that couples air–water exchange, phytoplankton uptake, and settling of organic matter as described by Dachs et al. (5). This parametrization has been successfully applied in previous studies (5, 9). On the other hand, k_{AW} has been estimated in the traditional manner, as the result of the transfer through two films at each side of the air–water interface (see refs 52 and 53), and using monthly mean sea surface temperature and wind speed determined by remote sensing. The assumption of a Weibull distribution of wind speed has been used to account for the nonlinear influence of this wind speed on k_{AW} (5).

Results and Discussion

Dry Aerosol Deposition and Net Air–Water Exchange Fluxes. Dry aerosol deposition and gross and net air–water exchange fluxes have been estimated using the measured atmospheric concentrations (16, 17) and remote sensing meteorological data, as reported in the Data Sources and Model Development sections discussed above. The measured latitudinal profiles of gas-phase concentrations of PCDD/Fs and PCBs and the measured and predicted aerosol-phase concentrations of PCDD/Fs and PCBs have been considered representative of the whole longitudinal width of the Atlantic when computing the average dry depositional fluxes.

The averaged latitudinal profiles of dry deposition and net air–water exchange fluxes for the Atlantic Ocean are shown in Figure 3. Results are shown for two PCDD/Fs homologue groups (Cl₂DDs and OCDF) and PCBs (PCB 52

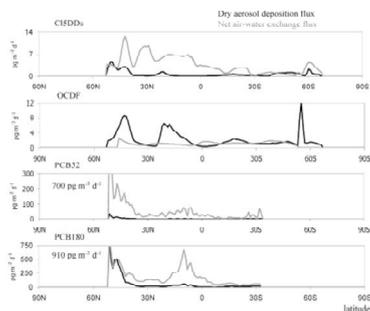


FIGURE 3. Latitudinally averaged profile of the dry aerosol deposition and net air-water exchange fluxes for Cl₄DDs, OCDF, PCB52, and PCB180 in the Atlantic Ocean. Zero values are shown for regions where satellite and/or POP measurements are not available.

and PCB 180) with different physical-chemical properties. There is a substantial variability in the calculated fluxes, highlighting the importance of considering spatially resolved data for global assessments of POP cycling. The dry deposition fluxes increase at mid-high latitudes, where temperatures are lower and contaminants tend to partition to a greater extent to aerosols. Wind speeds also tend to be higher at mid-high latitudes, contributing to enhanced turbulent driven deposition of accumulation mode aerosols (0.1–1 μm). Relatively high dry deposition fluxes are projected between 10° N and 25° N, the zone influenced by the Saharan-Sahel dust. Enhanced dry deposition fluxes are also estimated around 30° S, where there are high concentrations of marine aerosol. The assumption of uniformly distributed POPs over the aerosol size range may have some influence on these results. Presumably, organic carbon content in dust aerosol is low, and therefore this could mean that the fluxes presented here in dust outflow regions are overestimated. However, dust concentrations are significantly underestimated by satellite retrievals, as discussed above, and this could counteract the assumption on OC content in large aerosols. Conversely, marine aerosols may have very low concentrations of soot, and therefore this would lead to an overestimation of aerosol-phase concentrations of PCDD/Fs, but not of PCBs, and the associated dry aerosol deposition fluxes. Further research is needed on gas-particle partitioning of POPs for different types of aerosols in order to improve the accuracy of deposition estimates.

In contrast to the dry deposition flux, net air-water exchange shows a distinct latitudinal profile. The diffusive air-water exchange flux is mainly driven by temperature, wind

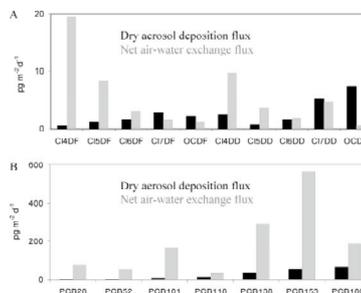


FIGURE 4. Comparison of mean dry aerosol deposition and air-water exchange fluxes for PCDD/Fs homologue groups (A) and PCBs (B) for the Atlantic Ocean.

speed, and sinking fluxes, the latter being favored in areas of high primary productivity (3). PCBs also exhibit relatively high air-water exchange fluxes at high latitudes, due to the combined effect of wind speed and primary productivity. In the NH, greater fluxes are also driven by higher gas- and aerosol-phase concentrations due to the proximity of sources. The percentage contribution of the dry aerosol deposition flux to the total depositional flux (i.e., dry aerosol deposition + net air-water exchange) is shown for selected PCBs and PCDD/Fs in Table 1. It varies from 2 to 27% and from 4 to 71% for PCBs and PCDD/Fs, respectively, with higher contributions at high latitudes and for the less volatile POPs.

Average dry aerosol deposition and net air-water exchange fluxes for the Atlantic Ocean are shown in Figure 4 for all the PCDD/Fs and selected PCB congeners. Averaged dry aerosol deposition fluxes are in the order of 1–7 pg m⁻² d⁻¹ for PCDD/Fs and 2–64 pg m⁻² d⁻¹ for PCBs. Net air-water exchange fluxes were more than 20 times higher than dry aerosol deposition fluxes for Cl₄DD/Fs but decreased with increasing chlorination level. For Cl₁₋₃DD/Fs, dry aerosol deposition dominates over the net air-water exchange flux. By contrast, averaged net air-water exchange was higher than the dry aerosol deposition flux for all PCBs. This is consistent with the higher fraction of PCBs in the gas phase and the affinity of PCDD/Fs to soot aerosol carbon. An important spatial variability was encountered: although air-water exchange is the main transfer route from the atmosphere to oceans for PCBs, this was not the case in some regions (see discussion below). If the gross gaseous absorption flux is considered instead of the net air-water exchange (absorption – volatilization), then its average magnitude to the Atlantic Ocean would be about 3–5-fold higher than the air-water exchange flux for PCBs and 2–3-fold higher for PCDD/Fs

TABLE 1. Averaged Percentage of Dry Aerosol Deposition Flux to the Atlantic versus Sum of Net Air-Water Exchange Flux and Dry Aerosol Deposition Fluxes

Fdd*100/(Fdd+Faw)	(61° N, 1° E)–(75° S, 20° W)			(52° N, 1° E)–(24° S, 20° E)		
	Cl ₄ DDs	Cl ₃ DDs	OCDF	PCB52	PCB101	PCB180
60° N–90° N	NM ^a	NM ^a	NM ^a	NM ^a	NM ^a	NM ^a
30° N–60° N	17	59	71	4	5	27
0° –30° N	4	14	66	2	3	10
30° S–0°	17	27	47	3	4	13
60° S–30° S	39	55	46	6	7	23
90° S–60° S	22	ND ^b & NM ^a	ND ^b & NM ^a	NM ^a	NM ^a	NM ^a

^a NM: not measured. ^b ND: not detected.