Latitudinal and seasonal capacity of the surface oceans as a reservoir of polychlorinated biphenyls

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“Capsule”: Model calculations estimate the latitudinal and seasonal storage capacity of the surface oceans for PCBs.

Abstract

The oceans play an important role as a global reservoir and ultimate sink of persistent organic pollutants (POPs) such as polychlorinated biphenyl congeners (PCBs). However, the physical and biogeochemical variables that affect the oceanic capacity to retain PCBs show an important spatial and temporal variability which have not been studied in detail, so far. The objective of this paper is to assess the seasonal and spatial variability of the ocean’s maximum capacity to act as a reservoir of atmospherically transported and deposited PCBs. A level I fugacity model is used which incorporates the environmental variables of temperature, phytoplankton biomass, and mixed layer depth, as determined from remote sensing and from climatological datasets. It is shown that temperature, phytoplankton biomass and mixed layer depth influence the potential PCB reservoir of the oceans, being phytoplankton biomass specially important in the oceanic productive regions. The ocean’s maximum capacities to hold PCBs are estimated. They are compared to a budget of PCBs in the surface oceans derived using a level III model that assumes steady state and which incorporates water column settling fluxes as a loss process. Results suggest that settling fluxes will keep the surface oceanic reservoir of PCBs well below its maximum capacity, especially for the more hydrophobic compounds. The strong seasonal and latitudinal variability of the surface ocean’s storage capacity needs further research, because it plays an important role in the global biogeochemical cycles controlling the ultimate sink of PCBs. Because this modeling exercise incorporates variations in downward fluxes driven by phytoplankton and the extent of the water column mixing, it predicts more complex latitudinal variations in PCBs concentrations than those previously suggested.

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1. Introduction

The oceans play an important role in controlling the environmental transport, fate and sinks of persistent organic pollutants (POPs) at regional and global scales (Wania and Mackay, 1996; Dachs et al., 2002). Even though POP concentrations in the open ocean are lower than those observed in coastal areas (Iwata et al., 1993; Dachs et al., 1997a; Schulz-Bull et al., 1998), the large oceanic volumes imply that they may represent an important inventory of POPs. This has been confirmed in budgets performed for some marine regions, such as the Western Mediterranean, and may be true for the global oceans (Dachs et al., 1997a; Tolosa et al., 1997).

Wania and Mackay (1996) suggested that temperature plays a significant role in determining the transport and sinking of POPs in the oceans at the global scale, through the processes of cold condensation, global distillation and latitudinal fractionation. This would result in an inverted concentration gradient of POPs, with low concentrations in the tropics and high concentrations in the polar regions. On the other hand, less volatile compounds are deposited close to their sources, while more volatile compounds travel further toward the poles, where they deposit preferentially due to lower temperatures. Therefore it has been suggested that temperature could largely explain the oceanic concentrations of POPs due to its influence on air–water exchange and other partitioning processes (Wania and Mackay, 1996).
However, due to the hydrophobic character of POPs, the spatial and temporal variability in the distribution of water column organic matter has an important influence on the oceanic inventory of POPs. Recently, it has been shown that phytoplankton uptake and settling of particulate matter is a driver of the oceanic sink of POPs such as polychlorinated biphenyls (PCBs) and dibenzo-p-dioxins and-furans (PCDD/Fs) (Dachs et al., 1999, 2000, 2002; Skei et al., 2000; Wania and Daly, 2002) and that the deep ocean is an important global sink for the more hydrophobic POPs (Wania and Daly, 2002). Besides the role that organic matter plays on the settling of POPs, no assessment exists of the potential influence of the spatial variability of organic matter and other biogeophysical variables on the capacity of the surface oceans as a reservoir of POPs. The physical and biogeochemical variables with potential influence on the oceanic inventory of POPs, such as phytoplankton biomass and mixed layer depth, show an important spatial and seasonal variability which presumably affects the cycling and long term fate of POPs.

Soil and vegetation organic matter, such as forested surfaces, has traditionally been considered in models that study the global distribution of POPs in terrestrial environments (Eisenberg et al., 1998; Scheringer et al., 2000; Wania and McLachlan, 2001). These studies have shown that terrestrial organic matter has an important influence on the dynamics and inventory of POPs. Therefore, it seems logical that high productivity oceanic areas may exert an important influence on the global distribution of POPs. Specifically, this work will be focused on POPs, such as PCBs, that are found preferentially in the gas-phase (Van Drooge et al., 2002).

The objectives of this work are to study the influence of environmental variables such as temperature, biomass and mixed layer depth on the reservoir capacity of PCBs by the surface oceans. The role of settling fluxes driven by enhanced phytoplankton productivity is assessed as a key factor affecting the global oceanic inventory of PCBs. The results are compared with those predicted by the global distillation theory under equilibrium conditions. Finally, the predicted inventory of PCBs in the surface ocean is compared with that reported in soils.

2. Data sources and field sampling

2.1. Physical and biogeochemical data

The global distribution of sea surface temperature (SST), chlorophyll $a$ concentrations, and the mixed layer depth ($MLD$) were assessed as potential variables affecting the reservoir capacity of oceans on a global scale. Data on their global distribution and variability were obtained by remote sensing from satellites and climatological datasets. SSTs were obtained from the Along Track Scanning Radiometer (ATSR) installed in the European Space Agency ERS-2 satellite (ATSR project web page http://www.atsr.rl.ac.uk/). SST images consist of monthly averaged data with a resolution of a half degree and an accuracy of $+/−0.3$ K.

Chlorophyll $a$ concentrations were estimated from fluorescence signals obtained from the Sea-viewing Wide Field-of-view Sensor (SeaWIFS) mission funded by NASA's Mission To Planet Earth (MTPE) Program (http://seawifs.gsfc.nasa.gov/SEAWIFS.html). Data are averaged monthly at $1° \times 1°$ resolution and an estimated error of $15\%$. Chlorophyll $a$ concentrations allow an estimation of the spatial and seasonal phytoplankton biomass distribution in the surface mixed layer.

The Samuels and Cox monthly global climatologies of the $MLD$ (prepared from the NOAA database) were obtained from the National Center for Atmospheric Research website (http://dss.ucar.edu/catalogs). $MLD$ data sets were available at a $1° \times 1°$ resolution. The atmospheric mixing layer ($AML$) corresponding to the marine boundary layer was assumed to be constant and equal to $1000$ m (Van Drooge et al., 2002). Even though this assumption may not be realistic in some regions, this assumption does not modify the conclusions of this study as discussed below. The present study is based on monthly values obtained from averaging the values corresponding to three consecutive years (1998, 1999, 2000) in order to obtain a climatological-like data set of biogeophysical variables.

2.2. Latitudinal profiles of physical and biogeochemical variables

Latitudinally averaged profiles of SST, chlorophyll $a$ and $MLD$ values for two representative months (January and July), are shown in Fig. 1.

In contrast to the smooth temperature profile (Fig. 1a), the latitudinal profile of chlorophyll $a$ concentrations (Fig. 1b) shows substantial variability, with pronounced and changing gradients over the whole profile, particularly at mid-high latitudes. Chlorophyll $a$ (Fig. 1b) exhibits the patchiness usually encountered in biological variables, corresponding to a non-uniform spatial distribution of phytoplankton biomass (Valiela, 1995). Seasonality is higher than for temperature: in January there is more phytoplankton biomass in the southern oceans, whereas in July productivity increases in high latitudes of the northern hemisphere.

The extend of the $MLD$ (Fig. 1c) largely determines the nutrient supply within the photic zone and how deeply the phytoplankton is carried by vertical mixing of water (Valiela, 1995). The $MLD$ is greater in zones with formation of deep water and poor water column stratification, such as the North Atlantic ocean in winter (Apel, 1990). The latitudinal profile of the $MLD$ has a stronger seasonality than temperature and chlorophyll $a$. However, along and around the equator, $MLD$ values remain fairly constant all year round.
The extent of the *MLD* may influence the vertical transport of PCBs, an issue that has not been studied in detail, so far. For example, a large *MLD* would cause PCBs to be in contact with the deep layers of the ocean. In contrast, a shallow *MLD* would cause concentrations in surface water to increase as a result of air–water exchange (Dachs et al., 1999).

Due to the observed seasonality and spatial variability of the physical and biological data, temporal and spatial changes in the capacity of the surface oceans as a reservoir of PCBs can be expected.

**2.3. Field measurements of atmospheric PCB concentrations**

Gas phase measurements of PCB concentrations have been reported for a north–south Atlantic transect from Germany to Chile (46N–46S) during the fall (October–December) of 1990. Details on the cruise route, sampling, and analytical procedures are given elsewhere (Schreitmüller et al., 1994). These atmospheric concentrations have been assumed to be representative of those found in the world oceans. Concentrations at latitudes higher than those reported in this study have been extrapolated assuming they decrease steadily towards the poles. This simplification is supported by the well known temperature dependence of gas phase concentrations, and compilations of measurements that show a decrease with latitude (Axelman and Gustafsson, 2002). The Arctic ocean is not covered in this study.

**3. Model description**

**3.1. Inventory of PCBs in the surface oceans**

The *inventory* (ng m$^{-2}$) of a given POP in the surface mixed layer of the oceanic water column is given by the sum of the concentration of the chemical in the dissolved ($C_W$, ng m$^{-3}$) and particulate phases ($C_P$, ng m$^{-3}$), multiplied by the mixed layer depth (*MLD*, m). Only the *MLD* of the water column is considered because it is the seawater mass under the direct influence of air–water exchange.

In most cases, phytoplankton uptake may control the aquatic partitioning of POPs (Swackhamer and Skoglund, 1991) and phytoplankton accounts for most of the organic matter in the photic water column (Gasol et al., 1997). Furthermore, it has been shown that the vertical and spatial variability of particulate-phase POPs such as PCBs and PAHs follow the phytoplankton biomass variability (Dachs et al., 1997 a,b). In addition, it is considered that $C_P$ is only relevant in the photic zone of the *MLD* (approximately 0–100 m). Therefore, the POP *inventory in the MLD* [ng m$^{-2}$] is given by:

\[
\text{INVENTORY} = (C_W + C_P) \times \text{MLD}
\]

For $\text{MLD} \leq 100$ m:

\[
\text{INVENTORY} = (C_W + C_P) \times 100
\]

For $\text{MLD} > 100$ m:

\[
\text{INVENTORY} = (C_W \times \text{MLD} + C_P \times 100)
\]

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Fig. 1. Latitudinally averaged profiles of the biogeophysical data in the Atlantic ocean, in January and July (climatological months): (a) Temperature, (b) Chlorophyll a concentrations, (c) *MLD*.

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The extent of the *MLD* may influence the vertical transport of PCBs, an issue that has not been studied in detail, so far. For example, a large *MLD* would cause PCBs to be in contact with the deep layers of the ocean. In contrast, a shallow *MLD* would cause concentrations in surface water to increase as a result of air–water exchange (Dachs et al., 1999).
where \( C_w \) (ng m\(^{-3}\)) and \( C_p \) (ng m\(^{-3}\)) are the POP concentrations of the dissolved and particulate (mainly phytoplankton) phases, respectively.

### 3.2. Ratio of maximum reservoir capacities (MRC)

The atmosphere is the main transport vector and diffusive air–water exchange the main input route to the water column for PCBs and other POPs which atmospheric occurrence is mainly in the gas phase (Dachs et al., 1999; Van Drooge et al., 2002). Indeed, the dry particle deposition of aerosol associated PCBs is negligible as an atmosphere ocean transfer process of PCBs (Dachs et al., 2002; Jurado and Dachs, unpublished data). Therefore, the maximum reservoir capacity (MRC) of the surface ocean to hold PCBs will be given by the ratio of the inventory in the surface ocean to the amount of PCBs in the atmospheric mixed layer.

\[
\text{MRC} = \frac{(C_w + C_p) \times MLD}{C_g \times AML} \quad \text{MLD} \leq 100 \text{ m} \quad (2)
\]

\[
\text{MRC} = \frac{C_w \times MLD + C_p \times 100}{C_g \times AML} \quad \text{MLD} > 100 \text{ m}
\]

where \( C_g \) (ng m\(^{-3}\)) is the POP gas phase concentration. Aerosol phase concentrations are assumed to be negligible in comparison to those in the gas phase and thus not contributing to the atmospheric inventory of PCBs. Estimated \( \text{MRC} \) values from Eq. (2) assume equilibrium between phases, consistent with a Level I fugacity model. This ratio allows an estimation of the total loading of a given PCB in the surface ocean water column, derived from an atmospheric concentration. It is important to stress that the inventory derived in this way will be an estimate of the maximum capacity of the surface oceans to hold PCBs.

#### 3.2.1. Level I fugacity model

The chemical is assumed to be at equilibrium between the gaseous, dissolved and particulate (mainly phytoplankton) phases. Specifically, PCBs in phytoplankton will move towards equilibrium with the dissolved phase; the latter will approach equilibrium with the gas phase. Air-water and water-phytoplankton exchange are viewed as reversible processes. Therefore, only the fugacity-driven processes of diffusive air–water exchange and phytoplankton uptake are considered. It is important to note that phytoplankton uptake is the first transfer step to food webs; the results presented here can therefore also be linked to consider the exposure of aquatic food webs to POPs.

The biological pump (sinking of phytoplankton associated pollutants) and oceanic circulation are processes that work against equilibrium in the ocean (Murray, 1992), causing the real inventory of PCBs in surface oceans to be presumably lower than that given by the \( \text{MRC} \) ratio. Vertical sinking of particle-associated pollutants is not considered in the level I predictions model because it is a non-fugacity driven process, but it will be considered in Section 5 below.

Equilibrium occurs when the fugacity of each phase matches the rest of the fugacities (Mackay and Paterson, 1981; Mackay, 2001). Fugacity can be regarded as the “escaping tendency” of a chemical substance from a given phase and has units of pressure. At equilibrium:

\[
 f_g = f_w = f_p
\]

where \( f_g \) (Pa) is the fugacity in the gas phase, \( f_w \) (Pa), in water and \( f_p \) (Pa), in the phytoplankton biomass. Fugacity is linearly related to concentration, by means of a fugacity “phase-specific” capacity constant: \( Z \). This term quantifies the capacity of a given phase to hold the chemical, so that toxic substances tend to accumulate in phases where \( Z \) is high. It is thus possible to write a fugacity–concentration relationship in each phase:

\[
\begin{align*}
 C_w &= f_w \times Z_w \times MW \times 10^9 \\
 C_g &= f_g \times Z_g \times MW \times 10^9 \\
 C_p &= f_p \times Z_p \times MW \times 10^9
\end{align*}
\]

where \( MW \) is the chemical molecular weight (g mol\(^{-1}\)) and \( Z_g \), \( Z_w \) and \( Z_p \) are the “fugacity capacities” (mol Pa\(^{-1}\) m\(^{-3}\)) in the gas, dissolved and phytoplankton phases, respectively, given by:

\[
\begin{align*}
 Z_g &= \frac{1}{R \times T} \\
 Z_w &= \frac{1}{H} \\
 Z_p &= \frac{r \times C_{OC} \times BCF}{H}
\end{align*}
\]

where \( R \) is the ideal gas constant (8.314 Pa m\(^3\) mol\(^{-1}\) K\(^{-1}\)), \( T \) is the temperature (K), \( H \) is the Henry’s law constant (Pa m\(^3\) mol\(^{-1}\)), \( r \) is the ratio between the amount of organic matter and the amount of organic carbon [kg\(_{\text{OM}}\)/kg\(_{\text{OC}}\)], \( C_{OC} \) is the concentration of organic carbon (kg\(_{\text{OC}}\) m\(^{-3}\)) and BCF is the PCB bioconcentration factor in phytoplankton (m\(^3\)/kg\(_{\text{phytoplankton}}\)).

The temperature dependence of the dimensionless Henry’s Law constant (\( H' \)) is described by the Gibbs–Helmholtz equation:

\[
\ln H' = \frac{\Delta H_H}{RT} + \frac{\Delta S_H}{R}
\]

where \( \Delta H_H \) and \( \Delta S_H \) (J mol\(^{-1}\)), are the enthalpy and entropy of the phase change from the dissolved phase to the gas phase and are independent of temperature. These are obtained from Bamford et al. (2000, 2002). Dissolved salts increase the value of \( H \). In the case of PCBs, studied
here, this effect can be parameterized using a salting out constant of 0.3 (Schwarzenbach et al., 1993) by:

$$H'_s = H' \times \exp \left(0.3 \times \frac{37}{58.5}\right)$$  \hspace{1cm} (9)

Chlorophyll a concentrations may be used to estimate the concentration of organic carbon (COC) and hence the phytoplankton biomass (Valiela, 1995; Gasol et al., 1997).

The ratio of chlorophyll to organic carbon is assumed to be 3 × 10⁻³ (kg algae chlorophyll/kgOC) (Jorgensen et al., 2000) and the value of r used is 2 kgOM/kgOC (Hedges et al., 2002). Phytoplankton is supposed to account for the majority of organic matter as discussed above.

The BCF is the ratio between the dissolved and phytoplankton PCB concentrations at equilibrium. In order to obtain the BCF, it should be noted that phytoplankton uptake is modeled using a two compartment system: first there is a fast adsorption to the phytoplankton surface (BCFₙ), then a diffusion into the matrix via partitioning (BCFₘ). Hence, the overall BCF is expressed as the sum of the BCFₙ and BCFₘ (Skouglund et al., 1996; Dachs et al., 1999, 2000; Del Vento and Dachs, 2002).

$$BCF = BCFₙ + BCFₘ$$  \hspace{1cm} (10)

BCFₙ and BCFₘ are related to compound physical-chemical properties, such as the octanol-water partition coefficient (KOW) at 298 K (Hawker and Connell, 1988).

$$\log BCFₙ(298) = 1.085 \times \log K_{OW} - 3.770$$
$$\log K_{OW} < 6.4$$  \hspace{1cm} (11)

$$\log BCFₘ(298) = 0.343 \times \log K_{OW} + 0.913$$
$$\log K_{OW} \leq 6.4$$

$$BCFₙ(298) = 233.61^* \log K_{OW} - 1084.05$$
$$\log K_{OW} < 6.3$$  \hspace{1cm} (12)

$$BCFₙ(298) = 398 \text{ if } 6.3 \leq \log K_{OW} < 7.0$$
$$BCFₙ(298) = -285.61^* \log K_{OW} + 2401.52$$
$$\log K_{OW} \geq 7.0$$

Temperature affects bioaccumulation and uptake kinetics by microorganisms. The influence of temperature on the bioconcentration factor is given in the following expression:

$$\frac{BCF(T)}{BCF(298)} = \exp \left[\frac{\Delta H_s}{R} \times \left(1 - \frac{1}{T} - 298\right)\right]$$  \hspace{1cm} (13)

where $\Delta H_s$ (kJ/mol) is the enthalpy of sorption, considered 35 kJ/mol for all the PCB compounds.

### 3.2.2. Air-water-phytoplankton equilibrium

$$\left[\frac{C_p + C_w}{C_g}\right]$$

A first approximation to the study of the variables affecting the MRC can be obtained from considering the ratio $(C_p + C_w)/C_g$ which shows the tendency of the chemical to partition in aquatic phases in comparison to the gas phase. This enables the influence of temperature and phytoplankton biomass to be assessed, without taking into account the variability associated with MLD and AML. Using Eqs. (3) and (4), and assuming equilibrium conditions, the following expression is inferred:

$$\frac{C_w + C_p}{C_g} = \frac{Z_w + Z_p}{Z_g}$$  \hspace{1cm} (14)

Replacing each fugacity capacity given in expressions (5), (6) and (7) gives:

$$\frac{C_w + C_p}{C_g} = \frac{1 + r \times C_{OC} \times BCF}{H'}$$  \hspace{1cm} (15)

### 3.2.3. Estimation of the ratio of maximum reservoir capacities (MRC)

For the estimation of MRC, in addition to temperature and phytoplankton biomass, two new variables need to be considered: the mixed layer depth in the water column (MLD) and the atmospheric mixed layer depth (AML). As discussed above, MLD is obtained from a climatological data set, whilst AML is assumed to be constant and equal to 1000 m (Van Drooge et al., 2002). This assumption does not affect the conclusions of this study since it is mainly focused on the marine side rather than the atmospheric. Thus, assuming equilibrium in all phases and combining Eqs. (2) and (15), MRC can be expressed as a function of the concentration of organic matter, temperature, MLD and the physico-chemical properties of the PCBs:

$$MRC = \frac{(Z_w + Z_p) \times MLD}{Z_g \times AML}$$
$$= \frac{(1 + r \times C_{OC} \times BCF) \times MLD}{H' \times AML}$$  \hspace{1cm} (16)

$$MLD \leq 100m$$
$$MRC \leq \frac{Z_w \times MLD + Z_p \times 100}{Z_g \times AML}$$
$$= \frac{MLD + r \times C_{OC} \times BCF \times 100}{H' \times AML}$$

$$MLD > 100m$$

### 4. Results and discussion

#### 4.1. Spatial and seasonal variability of $(C_w + C_p)/C_g$

For the calculations in this section, PCB 28 (3 chlorine atoms) and PCB 153 (6 chlorine atoms) have been
selected as indicative of PCBs with different physical–chemical properties. Fig. 2 shows the latitudinally averaged profiles of the maxima, minima and mean values of \( \frac{(C_w + C_p)}{C_g} \) for PCB 28 and 153 in the Atlantic ocean, in July. Examination of this ratio first, rather than studying MRC directly, facilitates an understanding of the latitudinal and seasonal behavior of MRC without considering the MLD, which sometimes masks the results due to its high variability in some regions. At first glance, Fig. 2 shows strong bimodal latitudinal trends, with greater values for this ratio at mid-high latitudes. A drop in the ratio is particularly pronounced in the subtropical regions. According to the cold condensation scenario, POPs volatilize from warm and temperate zones, undergo long range atmospheric transport and subsequently recondense at colder, higher latitudes (Wania and Mackay 1996). Thus, this theory predicts lower \( \frac{(C_w + C_p)}{C_g} \) values at low latitudes and higher \( \frac{(C_w + C_p)}{C_g} \) values at high latitudes. Therefore, the observed variability in Fig. 2 is only partially consistent with the temperature-driven latitudinal profiles suggested by the global distillation hypothesis. Indeed, the latitudinal profiles in Fig. 2 show a large difference between maxima and minima, notably at high latitudes, and important gradients and variability throughout the profile. The largest peak is not located in the highest latitude, as would happen if the ratio was solely governed by temperature; rather it is located around 60°N. Furthermore, at a given latitude, there is a 10 fold variability in the \( \frac{(C_w + C_p)}{C_g} \) values, mainly as a con-

Fig. 2. Maps and latitudinally averaged profiles of mean, maximum and minimum of \( \frac{(C_w + C_p)}{C_g} \) in July for: (A) PCB 28, (B) PCB 153.
sequence of phytoplankton patchiness. This important spatial variability can not be predicted taking into account solely the influence of temperature.

A closer examination of the averaged profile for PCB 28 (Fig. 2) shows variations between the maximum and minimum of a factor of 4–10, whereas for PCB 153 this is a factor of 100–1000. The increase of \((C_w + C_p)/C_g\) in mid-high latitudes is greater for the more hydrophobic PCB because of the major role of phytoplankton uptake.

The spatial, and specially the latitudinal variability of this ratio results from the dual variability in temperature and phytoplankton biomass. It is difficult to distinguish the effect of these two variables, because both increase at mid-high latitudes. An study of the latitudinal variability of temperature and phytoplankton biomass and their influence on the \((C_w + C_p)/C_g\) ratio has been performed.

4.1.1. Latitudinal variability of \((C_w + C_p)/C_g\) that can be attributed to the variability of input parameters

The influence of temperature and chlorophyll \(a\) on the latitudinal profile of \((C_w + C_p)/C_g\) was investigated by varying one parameter at a time, whilst maintaining the other constant. Hence, to assess the variability attributed to temperature, the latitudinal profile of \((C_w + C_p)/C_g\) was estimated by using the average value of chlorophyll \(a\) (0.75 mg/m\(^3\)) in the oceans (Dachs et al., 2002). Conversely, the variability attributed to phytoplankton biomass (i.e. chlorophyll concentration) was considered using a constant value of temperature of 286 K (Dachs et al., 2002). Results for PCB 28 and 153 are shown in Fig. 3a and b respectively. Chlorophyll \(a\) concentration produces a ‘spikiness’ in the latitudinal response, while temperature has a smoother effect latitudinally. An examination of individual plots suggests that for the more hydrophobic PCBs, the effect of biomass is stronger. On the other hand, temperature has a greater influence between 30 and 60°—in the zone where the gradient of \(T\) is greatest. Chlorophyll \(a\) concentration exerts its influence across the rest of the latitude range. Phytoplankton biomass is also responsible for the observed spatial patchiness. Thus, it is clear that temperature and compound physico-chemical properties are insufficient by themselves to predict the reservoir capacity of the surface oceans, especially for the more hydrophobic congeners.

4.1.2. Seasonal variability of \((C_w + C_p)/C_g\)

The predicted seasonal trends of \((C_w + C_p)/C_g\) are shown in Fig. 4a for PCB 153 in two contrasting areas of the north eastern Atlantic Ocean, one of high productivity (at 50°N), the other of low productivity (at 15°N). Average chlorophyll \(a\) concentrations and MLD in the two differentiate climatic regions are: 0.84 mg m\(^{-3}\) and 86.7 m (50°N); 0.47 mg m\(^{-3}\) and 22.1 m (15°N), respectively.

The seasonal trends at the mid-high latitude area follow a similar pattern to that of the chlorophyll \(a\) concentration, with a marked peak in spring (May–June) during the phytoplankton bloom. Lower values are predicted for the late summer, due to a decrease of phytoplankton biomass and higher temperatures. The area located in a sub-tropical region (15°N) is driven mostly by the effect of temperature, which has a dominant influence on \(H\). Indeed, the profile is little altered during the bloom and shows a negative correlation with temperature. The minimum occurs in July–August and the maximum in December–January. In this area, phytoplankton biomass is very low and thus its seasonal variability is also of limited importance (see Figs. 2 and 3). Conversely, in the high productivity region, the \((C_w + C_p)/C_g\) ratio is at a maximum during the spring phytoplankton bloom overwhelming the opposite influence of temperature.

4.2. Spatial and seasonal variability of the MRC

4.2.1. Seasonal trends of the MRC

Fig. 4b exhibits the annual profile of the MRC in a high productivity area around 50°N and in a low productivity area around 15°N. In the low productivity area, in early spring the MLD decreases, leading to lower MRC values during late spring and summer. However, for the high productivity area this decrease occurs after the spring phytoplankton bloom. Therefore, for the high productivity zone, MRC has a similar pattern to the seasonal variation in the amount of biomass and MLD, while for the low productivity area, MRC is largely driven by the effect of temperature and MLD.

4.2.2. Spatial variability of the MRC

Fig. 5 shows the spatially variability and the latitudinally averaged profiles of the MRC for PCB 28 and PCB 153. To illustrate the importance of seasonal variations of the MLD, the MRC calculated for January and July are compared. As observed for \((C_w + C_p)/C_g\) (Fig. 2), a bimodal MRC trend is observed, with higher values at mid-high latitudes. The MRC peaks around 60°, due to higher values of phytoplankton biomass and MLD at this latitude. Fig. 5 shows that the factors driving the MLD variability have a strong influence on the MRC which has not considered in previous studies. The longitudinal variability of MRC appears to be of relatively minor importance than when just the \((C_w + C_p)/C_g\) ratio is considered; however, it is still important. MRC patchiness due to phytoplankton biomass seems to be partially “damped” by the MLD when looking at the average latitudinal MRC values. MRC ratios are greater for PCB 153 than for PCB 28 (by about a factor of 10), in particular in mid-high latitudes. This is in agreement with the higher BCF values of PCB 153 than PCB 28.
4.2.3. Influence of MLD variability on the latitudinal profiles of the MRC

Using a constant value of MLD of 41 m (Dachs et al., 2002), the variability of MRC attributed to temperature and to chlorophyll $a$ concentration is very similar to that observed earlier for $(C_w + C_p)/C_g$. Therefore, only the variability attributed to MLD, as shown in Fig. 6, is assessed in this section—the MLD exhibits strong seasonality with higher values during early winter and minimum values during summer stratification of the water column. Therefore, MLD influence on MRC is also seasonally dependent and values for January and July are shown. MLD spatial variability drives a strong increase by a factor of 7–8 of MRC values during winter. This dependence is important at mid-high latitudes while it is not important at the subtropical region.

4.2.4. Settling fluxes decrease the water column reservoir of PCBs

The maximum potential inventory of PCBs in the oceanic mixed layer can be obtained by multiplying the MRC by the gas-phase concentrations. In this study, the PCB gas-phase concentrations measured in a north–south transect have been used as a reference (Schreitmüller et al., 1994). This maximum potential inventory, which is shown in Fig. 7, has been compared with that obtained from level III model that considers settling fluxes as a major removal process of PCBs from the water column. Indeed, recently, a level III model that assumes steady state conditions has been applied to the world’s oceans, to predict the processes controlling the oceanic sink of PCBs (Dachs et al., 2002). This model takes into account air–water exchange, phytoplankton uptake and settling of organic matter. Air–water fluxes ($F_{AW}$, ng m$^{-2}$ d$^{-1}$) can be modeled in the traditional manner:

$$F_{AW} = k_{AW} \left( \frac{C_g}{H} - C_w \right)$$

(17)

where $k_{AW}$ is the air–water mass transfer rate (m d$^{-1}$) that depends on temperature, wind speed and the phy-
sical–chemical properties of the pollutant. Fluxes of PCBs between water and plankton \( F_{WP,n \text{ gm}^2/C_0^2 \text{ d}/C_0^1} \) are given by the following equation:

\[
F_{WP} = k_{WP} C_w/C_0 \frac{k_d}{k_u} C_P \tag{18}
\]

where \( k_u \) (m \(^3\) kg\(^{-1}\) d\(^{-1}\)) and \( k_d \) (d\(^{-1}\)) are the uptake and depuration rate constants, respectively. The mass transfer coefficient between water and plankton, \( k_{WP} \) (m d\(^{-1}\)), depends on the mixed layer depth, the phytoplankton biomass, and the uptake constant (Dachs et al., 1999; Del Vento and Dachs, 2002).

Vertical fluxes of particles and associated PCBs are parameterized by:

\[
F_{sink} = k_{sink} \frac{k_d}{k_u} C_P \tag{19}
\]

where \( k_{sink} \) (m d\(^{-1}\)) is the mass transfer rate of sinking PCBs, related to the vertical flux of organic carbon.

In this model, the sequestration of PCBs by the ocean is viewed as an air–water–plankton-deep water exchange process. On a long-term basis and due to compound persistence, the air–water–plankton-deep ocean transport is assumed to be at steady state and therefore, \( F_{AW} \) equals \( F_{WP} \) and \( F_{sink} \). The system of Eqs. (17)–(19) is solved, making it possible to estimate the global variability of \( C_w, C_P \), and thus of the surface ocean inventory of PCBs. In this case, equilibrium conditions are not assumed and settling of PCBs associated with sinking organic matter is considered as the major removal process. Fig. 7 also shows the predicted surface ocean inventory using this level III model for PCB 28 and PCB 153.

![Fig. 4. Seasonal variation for PCB 153 in two areas of 2\( \times \)2 degree, one located in a high productivity region (around 50\(^{\circ}\)N, 0.91 mg chlorophyll/m\(^3\)), the other one in a low productivity region (around 15\(^{\circ}\)N, 0.09 mg chlorophyll/m\(^3\)): (a) \((C_w + C_p)/C_g\), (b) MRC.](image-url)
column inventory is predicted to be close to equilibrium for all PCB congeners.

5. Relative importance of the surface ocean as a reservoir of PCBs

Surface water inventories have been integrated for all the world oceans and for seven representative PCB congeners (PCBs 28, 52, 101, 118, 138, 153, 180) as predicted from the level III model. These inventories have been compared with those reported for soils at the global scale (Meijer et al., 2002) as shown in Fig. 8a. The concentrations and latitudinal distributions reported elsewhere (Schreitmüller et al., 1994) are consistent with other measurements of gas-phase concentrations made over the ocean and in oceanic islands (Iwata et al., 1993; Lohmann et al., 2001; Van Drooge et al., 2002) and presumably the uncertainty associated to these concentrations and the predicted inventory in the surface ocean is lower than a factor of two.

Fig. 5. Maps and latitudinally averaged profiles of MRC in January and July for: (A) PCB 28, (B) PCB 153.
The global PCB inventory in soils is greater than in the surface ocean for all congeners, but differences are more remarkable for the highly chlorinated PCBs. This suggests that the ocean is enriched in the lower chlorinated PCBs, which are not effectively removed by the settling of biogenic particulate matter. Conversely, the more hydrophobic congeners would become depleted in the water column due to efficient removal by settling particulate matter. Indeed, measured PCB profiles in soils are different from those predicted in surface oceans (Meijer et al., 2003; Dachs et al., 1997a,b). The inventories shown in Fig. 8 are for the surface ocean, i.e. above the MLD. However, the deeper ocean may contain a much greater inventory of PCBs, that remain to be quantified. In any case, oceanic deep water can be considered as a sink for PCBs since they will not move back to the atmosphere and cycle through the biogeo-sphere.

The relative contribution of the individual PCBs in the predicted surface water inventories integrated for all the world oceans has been compared with that obtained in other areas such as the North-Atlantic Ocean and the Mediterranean Sea (Dachs et al., 1997a; Schulz-Bull et al., 1998). For these field studies, the relative contribution of the measured PCBs in suspension ($C_p$) and in solution ($C_w$) has been considered. Results are shown in Fig. 8b. The PCB profiles derived here have similar trends to those reported for the Atlantic Ocean by Schulz-Bull et al. (1998). Some differences can presumably be attributed to variability of phytoplankton biomass in surface waters, causing variations in the partitioning and thus the congener specific PCB profile.

Samples for the Mediterranean Sea (Dachs et al., 1997a) were dominated by the tri- and tetra-substituted species, which is consistent with a large and rapid sinking of particle associated pollutants in this area and their closer proximity to land sources. Samples from Schulz-Bull et al. (1998) showed very high concentrations in suspension compared to those in solution, as a result of the relatively high suspended matter concentrations in the sampling area (Northern Atlantic Ocean).
6. Concluding remarks

The study of the biogeoophysical variables that control the maximum capacity of the oceans to hold POPs such as PCBs shows that in high productivity areas, phytoplankton biomass and the extend of the MLD are the most important parameters. Conversely, in oligotrophic areas, temperature and the MLD drive the MRC values. This study has shown that it is important to assess the fate and occurrence of POPs in marine environment taking into account the biogeochemistry of POPs, specially their interactions with biota which leads to an important spatial and temporal variability. The role of the extend of the MLD on the fate and occurrence of POPs is an issue that needs to be assessed in detail.

Furthermore, this study provides evidence that the surface ocean is enriched in the lower chlorinated PCBs, which are not effectively removed by the settling of biogenic particulate matter. This observation further support the hypothesis that long range atmospheric transport followed by air–water exchange and settling fluxes are key processes affecting the inventory and fate.
of PCBs in the surface oceans. Furthermore, at the global scale, it can be hypothesized that continent-ocean interactions may play an important role of the global dynamics of PCBs and be responsible for the differences observed between soil and seawater profiles (Fig. 8). However, further research is needed to better assess transport routes and to understand the interactions between continents and oceans in terms of POP occurrence and transport.

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