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BIOGEOCHEMICAL CONTROLS ON AIR-WATER EXCHANGE AND GLOBAL OCEANIC SINK OF POLYCHLORINATED BIPHENYLS AND POLYCHLORINATED DIBENZO DIOXINS AND FURANS

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Introduction

The long-range transport, persistence and global dynamics of persistent organic pollutants (POPs) have been issues of increasing concern during the last decade with the objective to understand their ultimate sinks and their impact on the biosphere. Air-water exchange plays a major role on the mobilization and dynamics of POPs at the global scale [1], but the implications of its coupling with biogeochemical processes such as phytoplankton uptake and settling of marine particulate matter has not been considered in detail [2, 3]. However, the potential importance of the deep ocean as a final sink of POPs has already been recognized [3, 4]. In the present study, field measurements of atmospheric polychlorinated biphenyls (PCBs), polychlorinated dibenzo dioxins and furans (PCDD/Fs) are combined with remote sensing estimations of oceanic temperature, wind speed and chlorophyll, to model the interactions between: air-water exchange, phytoplankton uptake and export of organic matter and POPs out of the mixed surface ocean layer. Finally the magnitude of the global oceanic sink and atmospheric deposition of PCBs and PCDD/Fs is estimated.

Methods and Materials

Field measurements of atmospheric concentrations of PCBs and PCDD/Fs were made during a North-South Atlantic Ocean transect (52N-72S) during the fall (October-December) of 1998. Large volumes of air were sampled (300-950 m3) using polyurethane foams (PUFs) and glass fiber filters (GFFs). PUFs and GFFs were extracted separately. After extraction and fractionation, PCDD/Fs and coplanar PCBs were analysed by HRGC-HRMS using an HP 6890 GC connected to a Micromass Autospec Ultima high-resolution instrument at a resolving power of 10,000 or more. The non-coplanar PCBs were analysed by HRGC coupled to an electron capture detector. Full details of the cruise route, sampling and analytical procedures are given elsewhere [5, 6].

Results and Discussion

Most PCDD/Fs and the more hydrophobic POPs showed higher concentrations at low latitudes than at mid to high latitudes, and higher concentrations in the Northern hemisphere, consistent with latitudinal emission distribution. The less chlorinated PCBs did not show such a decrease in concentrations at high latitudes, but displayed uniform atmospheric concentrations over the Atlantic Ocean [5, 6].

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After long-range atmospheric transport, POPs may be deposited to the open ocean by three processes: diffusive air-water exchange, dry particle deposition and wet deposition. As far as PCBs are concerned and for most PCDD/Fs, air-water exchange is the dominant air to water depositional process [7, 8]. The sequestration of POPs by the ocean can thus be viewed as an air-water-plankton-deep water exchange process. Air-water fluxes (F_{AW}, ng m^{-2} d^{-1}) can be modeled in the traditional manner:

$$F_{AW} = k_{AW}\left(\frac{C_A}{H'} - C_W\right) \qquad [1]$$

Where C_A and C_W are the dissolved and gas phase POP concentrations (ng m^{-3}) respectively, H' is the temperature corrected dimensionless Henry's law constant, and k_{AW} is the air-water mass transfer rate (m d^{-1}) that depends on temperature, wind speed and the physical-chemical properties of the pollutant. Fluxes of POPs between water and plankton (F_{WP}, ng m^{-2} d^{-1}) are given by equation [2]:

$$F_{WP} = k_{WP}\left(C_W - \frac{k_d}{k_u} C_P\right) \qquad [2]$$

where C_P is the POP concentration in phytoplankton (ng kg^{-1}), 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 (MLD, m), the phytoplankton biomass (B_P, kg m^{-3}), and the uptake constant [2, 9].

Vertical fluxes of particles and associated POPs can be parameterized by.

$$F_{Sink} = k_{Sink}\frac{k_d}{k_u}C_P \qquad [3]$$

where k_{Sink} (m d^{-1}) is the mass transfer rate of sinking POPs, related to the vertical flux of organic carbon. The global spatial and seasonal variability of k_{AW}, k_{WP} and k_{Sink} were determined using remote sensing estimations of temperature, wind speed and chlorophyll corresponding to the same time period of the sampling cruise, as reported elsewhere [10]. Values for H', k_u and k_d were selected from the literature [9]. On a long-term basis and due to the persistence of PCBs and PCDD/Fs, we can assume that the air-water-plankton-deep ocean transport is at steady state and therefore F_{AW}, F_{WP} and F_{Sink} are equal. C_A values were measured over the Atlantic Ocean and it is assumed that they are representative of open ocean conditions. Under these assumptions we can solve the system of equations [1-3] and estimate the global variability of C_W, C_P and F_{AW} for all the PCBs and PCDD/Fs. Figure 1 shows the spatial and latitudinal variability of the air-water fluxes for PCB180. F_{AW} is higher in highly productive areas such as in the upwelling areas off-Sahara, off-Namibia, off-Perú and in the Arabian Sea. This is true for the more hydrophobic POPs. Therefore, the global dynamics of semivolatile chemicals is strongly influenced by biogeochemical processes such as the biological pump (uptake + sinking) in addition to temperature. In fact, the relatively high values of F_{AW} at high latitudes (Figure 1) may not only be due to enhanced air-water exchange as a result of the low temperatures but also to the high primary productivity in these areas. The kinetically limiting step in air-deep ocean transport can be determined by comparing the mass transfer rates of each step.. Phytoplankton uptake is a fast process and thus k_{WP} will never be the limiting rate [2]. Figure 2 shows the comparison of k_{AW} and k_{Sink} for selected PCDDs. For these hydrophobic POPs and at low latitudes, k_{AW} is higher than k_{Sink} and therefore sinking of particulate organic matter is the limiting step. Conversely, at high latitudes, k_{Sink} is higher than k_{AW} and thus air-water exchange can not support the sinking of particle-associated POPs and there is a depletion of water column POP concentrations (C_W and C_P). The ratio of fugacity in air (f_A) to fugacity in water (f_W) is thus close to unity at low latitudes and significantly higher than one at high latitudes (Figure 2.C). Therefore, air-water and sinking fluxes at high latitudes are increased due to a greater air-water

gradient in concentrations driven by the high primary productivity in these areas. These results show the important role of biogeochemical processes to drive global dynamics and sinks of POPs.

The combination of experimental measurements of POPs, remote sensed data and modeling allows to estimate for the first time the global oceanic air-water exchange and sinking fluxes of POPs. For example, Figure 3 shows the integrated global fluxes for PCDD/Fs, which are higher for the low chlorinated congeners. The total air-water flux of PCDD/Fs for all the oceans is of c.a. 2990 kg y^{-1}, and thus it is higher than the estimated dry deposition (200 kg y^{-1}) and wet deposition (900 kg y^{-1}) global fluxes reported elsewhere [11]. However, the relative importance of dry deposition, wet deposition and diffusive air-water transport will be dependent on the PCDD/F congener specific physical-chemical properties and thus further research is needed to quantify dry and wet deposition at the global scale for individual PCDD/Fs.
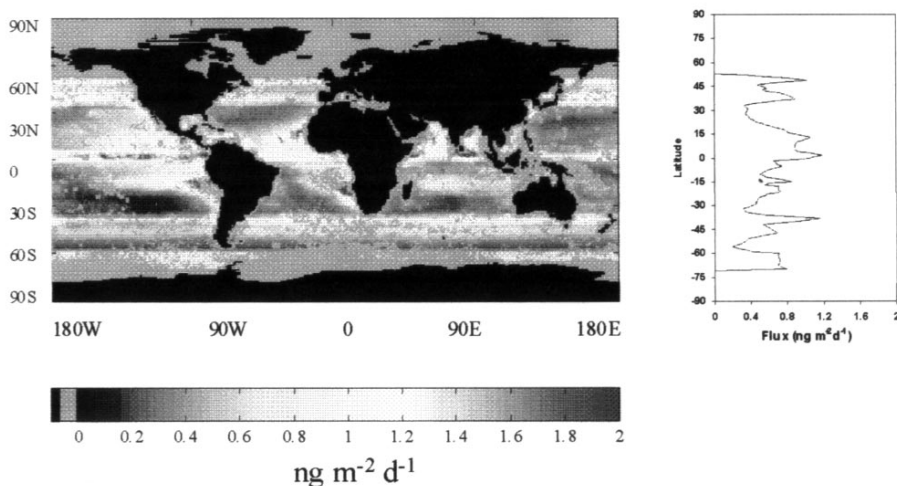

Figure 1. Global spatial variability and latitudinal profile of predicted air-water fluxes for PCB 180.
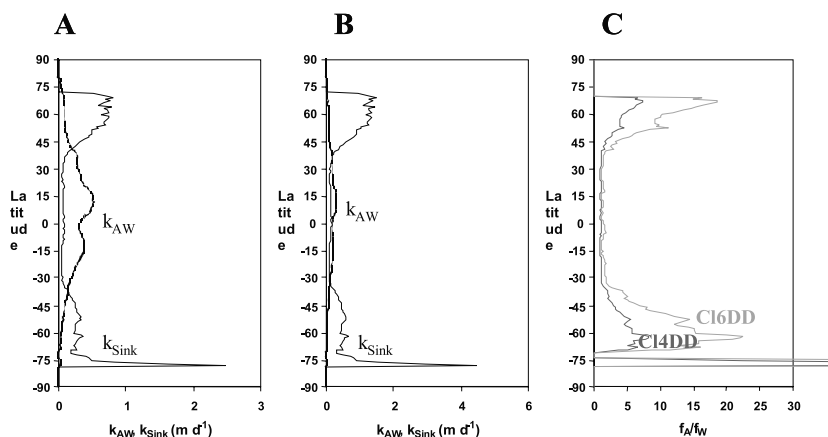

Figure 2. Comparison of k_{AW} and k_{Sink} for A) tetra chlorinated dibenzo dioxins (Cl4DD), B) hexa chlorinated dibenzo dioxins (Cl6DD) and C) fugacity ratios for Cl4DD and Cl6DD.

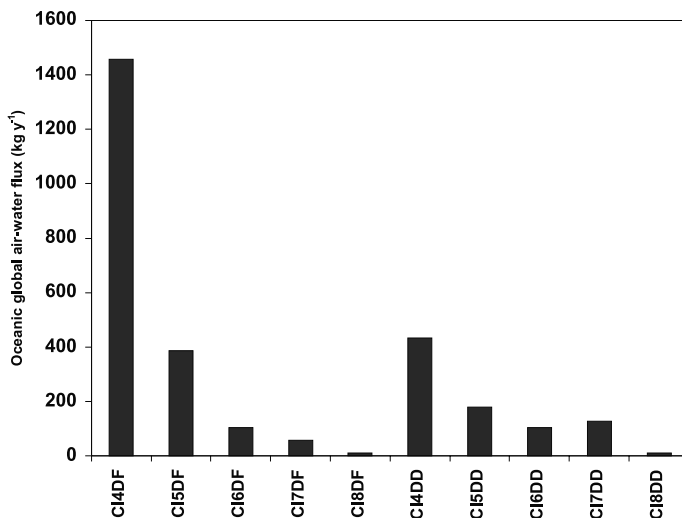# ENVIRONMENTAL TRANSPORT AND FATE

Figure 3. Global atmosphere-ocean fluxes of PCDD/Fs.

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