Ocean-Atmosphere Exchanges of Persistent Organic Pollutants on the Atlantic Ocean

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3.1 Background Information

Persistent Organic Pollutants (POPs), also known as Persistent Bioaccumulable Toxic chemicals (PBTs), are bioaccumulable compounds of prolonged environmental persistence and are susceptible to long-range atmospheric transport. They have been detected in all the environmental compartments, even in remote areas such as the open ocean and the polar regions, where POPs have never been manufactured or used. Furthermore, once they appear in the environment they do not degrade. Instead, they recycle and partition between the major environmental media, and are an environmental concern since their toxic effects do not disappear, and their control is difficult. Their physicochemical properties, such as the high lipid/organic solubility, result in their bioaccumulation in lipid-rich tissues and ‘bio-magnification' through the food chain. Even at low concentrations they are toxic to humans and wildlife, with suspected effects including carcinogenesis, immune dysfunction, neurobiological disorders and reproductive and endocrine disruption.

POPs comprise man-made organo-halogenated compounds (e.g. pesticide POPs such as DDT, industrially produced POPs such as polychlorinated biphenyls (PCBs) or POPs that are unintended byproducts such as polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) and other chemicals that can, in part, be biogenic such as polycyclic aromatic hydrocarbons (PAHs). In particular, man-made POPs were initially produced and used in the 1940s. During the 1960s and 1970s, the use of certain POPs in industry or as pesticides increased dramatically. The first political regulations for the production and use of POPs dates from the late 1970s. Since then, a number of politically-binding regulations have entered into force to reduce or eliminate their emissions: the Convention on Long-Range Transboundary...
Air Pollution on POPs, the Stockholm Convention on POPs, and, at the European Level, the Water Framework Directive.

Despite regulations, they still cycle between the different environmental compartments and there are non-controlled sources as well. For example, high concentrations of PCBs have been reported in arctic wildlife and breast milk. This is of special concern, not only because those contaminants were already banned in the late 1970s, but also because of the distance from the source where those pollutants were produced. There is thus a global occurrence of these contaminants and an urgent need to control their levels in the environment. Sampling of POPs, however, is time-consuming and expensive compared to many other contaminants. In this context, global models are a valuable tool to predict and understand the distribution of POPs. Satellite data, with their global synoptic coverage, can provide environmental input data to global POPs models, as we will see later.

To understand how we can use remote sensing data to model the global distribution of POPs, we provide here a short explanation of the partitioning of POPs in the different environmental media. Because both atmosphere and oceans are critical compartments in the global distribution and cycling of POPs, the analysis will focus in the ocean-atmosphere exchanges of POPs. Atmospheric emissions and subsequent long-range transport have proven to provide a mechanism to distribute POPs widely through the global environment. In fact, atmospheric deposition of POPs may be the major process by which they impact remote oceans and other pristine environments. On the other hand, the oceans are also critical in the global cycling of those pollutants; their large volumes imply that they may represent an important inventory of POPs.

Figure 3.1 shows a diagram of the major processes affecting the transfer of POPs between the atmosphere and the ocean. In the atmosphere, POPs partition between the gas and aerosol phases and they may then be removed by three processes: dry deposition of aerosol-bound pollutants, diffusive gas exchange between the atmosphere and the ocean, and scavenging by rain (either from gas or particulate phases), the latter termed wet deposition. In the water column, POPs can be found either dissolved or sorbed to particulate organic matter. Dissolved POPs can revolatilize back to the atmosphere or they can stay in the water column and become bioavailable, i.e. they can be incorporated into the biota by passive diffusion. POPs sorbed to particulate organic matter cannot revolatilize back to the atmosphere, but can be deposited by gravity or sinking. In both particulate and dissolved phases, they are subject to turbulent mixing throughout the water column. Finally, in each medium, POPs are subject to degrade, but those fluxes are generally considered negligible. By means of simplification, no lateral advection of contaminants is considered, which is an assumption generally accepted in the open ocean, where contaminants enter primarily via atmospheric deposition.

The processes affecting the transfers of POPs between the atmosphere and the ocean are evaluated quantitatively by means of fluxes ($F \text{ [ng m}^{-2} \text{ s}^{-1}]$), whose
simplified mathematical formulation is presented next. Advective processes, where contaminants are transported by means of directed motion, such as dry deposition, wet deposition and sinking, are governed by:

\[ F_{\text{advective}} = vC \]  

(3.1)

where \( v \) [m s\(^{-1}\)] is the advective velocity and \( C \) [ng m\(^{-3}\)] is the concentration of the chemical.

Diffusive processes, such as air-water exchange or turbulent flux, where contaminants are transported by random motion, are governed by Fick’s First Law:

\[ F_{\text{diffusive}} = -D \frac{\partial C}{\partial x} \]  

(3.2)

where \( D \) [m\(^2\) s\(^{-1}\)] is the molecular diffusivity and \( \partial C/\partial x \) is the gradient of concentrations in the x direction, along which the change of concentration of the contaminant occurs. The mathematical formulation of diffusion becomes more complex if the transport occurs between two media, as would be the case of the diffusive transport across the air-water interface. The resultant flux is then a combination of molecular and turbulent diffusion.

The last type of process, the degradation process, produces a loss in the system, and is characterized by a first order decay rate, \( k_{\text{degr}} \) [s\(^{-1}\)].

\[ F_{\text{transformation}} = h k_{\text{degr}} C \]  

(3.3)
where \( h \) [m] is the height of the volume where degradation is acting.

It is important to note that the magnitude of the contaminant fluxes is a function of the measured concentration, physicochemical parameters, and environmental conditions. The environmental conditions do not only determine the parameters \( v \), \( D \) and \( k_{\text{deg}} \), from Equations 3.1 to 3.3, they also influence the ratio of contaminant concentrations between two different phases of equilibrium. This ratio is termed the *equilibrium partition coefficient* and it is essential in the modelling of POPs. For example, the gas-particle partition coefficient \( K_p \) will allow us to calculate the concentration of a certain POP in its aerosol phase, knowing its concentration in the gaseous phase and assuming equilibrium conditions, which is a common assumption since these compounds are continuously seeking to equilibrate between the different reservoirs.

This case-study shows an example of the application of satellite data to estimate the spatial and temporal distribution of atmospheric-ocean fluxes of POPs in the Atlantic Ocean. It has been developed in detail in various publications (Dachs et al. 2002; Jurado et al. 2004; 2005; 2008) and it is based on the previous work of Dachs et al. (2002) and Simó and Dachs (2002). Essentially, satellite retrieved parameters and air measured concentrations (gaseous and aerosol phases) in two north-south campaigns across the Atlantic (Lohmann et al. 2001; Jaward et al. 2004) have been coupled in a 0D (i.e. zero-dimensional), spatially resolved, box model. A 0D model means, for example, that the vertical variation of the fluxes is not accounted for. A box model means that the system has been subdivided into well-mixed and interconnected compartments. The model was applied using monthly means of satellite data and assuming that measured atmospheric concentrations are constant in time.

Satellite-based environmental data correspond to monthly climatological means (average 2001 – 2003) of *Level 3* data with global coverage and resolutions of 1°x1° or 0.5°x0.5°, presented in greater detail below. *Level 3* refers to data that is designed for the end user, which has been calibrated with *in situ* observations and data assimilation techniques.

### 3.2 Satellite Data Used

#### 3.2.1 Wind speed distributions at 10m above the surface of the sea

The surface wind speed was used in this study (\( u_{10} \), m s\(^{-1}\)). Values were obtained from the NOAA Special Sensor Microwave/Imager (SSM/I) at a resolution of 1°x1° and an accuracy of \( \pm 2 \) m s\(^{-1}\) ([http://lwf.ncdc.noaa.gov/oa/satellite/ssmi/ssmiwind.html](http://lwf.ncdc.noaa.gov/oa/satellite/ssmi/ssmiwind.html)).
3.2.2 Aerosol parameters over the oceans

Aerosol values at a resolution of 1°x1° 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). In particular, we used the effective radius (\(r_{\text{eff}}, \mu m\)) and its standard deviation (which provides information about the size distribution of aerosols), the aerosol optical depth (AOD) and its standard deviation (related to the aerosol density in the atmosphere), and the fraction of optical depth corresponding to submicron aerosols (\(\eta, [0-1]\)). The approximate accuracy is \(\pm 0.1\mu m\) for \(r_{\text{eff}}\), \(\pm 0.03\times\text{AOD}\) (or \(\pm 0.05\times\text{AOD}\) in dust regimes), and 25% for \(\eta\). MODIS aerosol retrieved measurements refer to values integrated over the air column and they refer to the size range detected by the instrument (aerosol diameters from 0.1 to 20 \(\mu m\)). This information is important to derive aerosol dry deposition velocities from satellite data (Jurado et al. 2004).

It should be pointed out that deriving aerosol sizes or concentrations from remote sensing measurements has a higher uncertainty than other variables such as wind speed, SST and \(p_0\) used in this study. Until recently, MODIS was the only sensor that gave information about aerosol sizes. This area of research is currently undergoing rapid development, and several satellite-based light imaging radars (lidars) are being launched (e.g. CALIPSO from NASA), providing information about the vertical structure of aerosol plumes, which is not available from MODIS data.

3.2.3 Precipitation data

Values of monthly rainfall rates (\(p_0, [\text{mm month}^{-1}]\)) and the fractional occurrence of precipitation (\(f, [0-1]\)) were obtained from SSM/I NOAA at a resolution of 1°x1° (http://www.ncdc.noaa.gov/oa/satellite/ssmi/ssmiprecip.html). Determination of rainfall by passive microwave sensors, such as SSM/I, may be underestimated during low rainfall periods and overestimated during wet periods, leading to some inaccuracies in the tropics. However, rainfall retrieval over the ocean from SSM/I represents the best compromise between estimation accuracy and spatial data coverage. Uncertainty is about 15 to 30% when compared to rain gauge data sets.

A novelty of the use of precipitation data in wet deposition modelling of POPs has been the consideration of the influence of the frequency of rain (\(f\)). The instantaneous flux of contaminants scavenged by rain may be substantial in a month with a low frequency of rain and a high rainfall rate. The methodology developed is further described in Jurado et al. (2005).

3.2.4 Sea Surface Temperature (SST, [K])

Values were obtained from the Along Track Scanning Radiometer (ATSR) on board the European Space Agency ERS-2 satellite (http://www.atsr.rl.ac.uk/). SST im-
ages consist of monthly averaged data with a resolution of 0.5°x0.5° and an accuracy of ±0.3K.

### 3.2.5 Chlorophyll-α concentration (chl-α, mg m⁻³)

This was estimated from reflectance signals obtained from NASA’s Sea-Viewing Wide Field-of-view Sensor (SeaWiFS) [http://www.csc.noaa.gov/crs/rs_apps/sensors/seawifs.htm](http://www.csc.noaa.gov/crs/rs_apps/sensors/seawifs.htm). The resolution is 1°x1° and accuracies are around the 15%. This data allows the estimation of the phytoplankton biomass distribution in the surface mixed layer.

### 3.3 Demonstration Section

In this section we present the values of dry deposition flux, latitudinally-averaged for the Atlantic, together with satellite global maps of data that have a potential effect in the magnitude of the flux. Visually-based interrelations between this flux and that pertaining to the satellite data are explained, so that one can acquire the skills required to use the satellite images to understand better the latitudinally-averaged fluxes of POPs.

**Figure 3.2**  Averaged latitudinal profile of the dry aerosol deposition fluxes for Cl5DDs and Cl7DDs over the Atlantic Ocean, for the period October-December 1998.

As a reminder, the dry aerosol deposition flux is the deposition of aerosol-bound contaminants in the absence of rain. Figure 3.2 depicts an example of a latitudinally-averaged profile of dry deposition flux over the Atlantic for two
reference compounds, the penta-dibenzo-p-dioxin (Cl5DDs) and the hepta-dibenzo-
p-dioxin (Cl7DDs). The flux has been estimated using the methodology presented in
the previous section, but developed in detail in Jurado et al. (2004). An example of
measured air concentration data is depicted in Figure 3.3.

For the interpretation of Figure 3.2 we provide the following satellite images: sea
surface temperature (SST) (Figure 3.4), indicative of the temperature of the air close
to the water surface, the effective radius (r_{eff}) (Figure 3.5), defined as the weighted
integral of the volume-surface ratio and indicative of the size of the aerosol, the
aerosol mass concentration derived from the aerosol optical depth (Figure 3.6)
(Gasso and Hegg 2003), and the wind speed at a height of 10 m (u_{10}) (Figure 3.7).

As a first step to better understand the way that the dry aerosol deposition
fluxes are connected to the environmental data provided in Figures 3.4 to 3.7, it is
important to take into account the exact parameterization of this flux:

\[ F_{DD} = V_D C_{AER} \]  \hspace{1cm} (3.4)

where \( F_{DD} \) [ng m\(^{-2}\) s\(^{-1}\)] is the dry aerosol deposition flux, \( V_D \) [m s\(^{-1}\)] denotes the
aerosol overall dry deposition velocity and $C_{AER}$ [ng m$^{-3}$] is the POP aerosol-phase

**Figure 3.4** Global distribution of Sea Surface Temperature (SST) in January (climatological monthly mean of 1998 - 2000).

**Figure 3.5** Global distribution of effective radius ($r_{eff}$) over the oceans in November (climatological monthly mean of 1998 - 2000).
Figure 3.6  Global distribution of the aerosol mass concentration over the oceans in November (climatological monthly mean of 1998 – 2000). Derived from MODIS Aerosol Optical depth parameter, and the algorithm developed in Gasso and Hegg (2003).

From Equation 3.4 one should note that the dry aerosol deposition flux is directly proportional to the POP-aerosol-phase. Indeed, major dry deposition fluxes will be found in regions with major amounts of contaminants in the aerosol phase. The tendency to be in the aerosol-phase instead of the gas-phase is highly dependent on the air temperature, so that a lower air temperature will cause a higher partition to the aerosol phase. A map of SST, representative of the temperature of the air above the ocean surface, provides information of the regions over the oceans with a higher proportion of contaminants in the aerosol phase i.e. the temperate regions at higher latitudes.

The sea surface temperature (Figure 3.4) cannot be the only variable affecting the latitudinal trend in the fluxes from Figure 3.2, because it follows a smooth increase towards higher latitudes, while the fluxes depict an important variability. Other environmental variables, with a higher patchiness, should affect the magnitude of the fluxes. We envisage that the effective radius (Figure 3.5), aerosol mass concentration (Figure 3.6) or the wind speed (Figure 3.7) could contribute because their global distribution presents a higher variability than the SST.

How do Figures 3.5 to 3.7 combine to explain the fluxes in dry deposition of
Figure 3.7 Global distribution of the wind speed ($u_{10}$) over the oceans in November (climatological monthly mean of 1998 – 2000).

POPs? The answer is found in the next variable, not yet assessed in equation 3.4, the overall dry deposition flux $v_D$. The $v_D$ is greatly influenced by the aerosol size, by the atmospheric turbulent diffusion and by the atmospheric growth of particles at a high humidity. In particular, $v_D$ will increase with the particle diameter and the wind speed for diameters $>0.1 \ \mu m$, governed by gravitational settling. Also, a high concentration of aerosol in the atmosphere will increase the dry deposition velocity. Knowing this information, it is possible to relate the large increase in the fluxes around 15$^\circ$S to an increase of the effective radius, indicative of the size of aerosol particles, or the aerosol mass concentration in the Atlantic around this latitude. Furthermore, we can relate the peaks in the dry deposition fluxes around 60$^\circ$S to strong winds in the Southern Ocean.

We end this section by explaining the differences in the fluxes of the two depicted contaminants: Cl5DDs and Cl7DDs. This is an example of how physico-chemical properties of the chemical compounds affect the fluxes. We see that the relative increase of dry deposition fluxes of the Cl7DDs in higher latitudes is greater than for Cl5DDs. This is because Cl7DDs sorb stronger to the organic matter of the aerosol, causing a major relative presence of those compounds in the aerosol phase. As a general rule, compounds with higher molecular weight will have less solubility in water, a higher affinity to organic matter and a lower vapour pressure.
3.4 Training and Questions

Q 1: Do you see any links between the flux of wet deposition (Figure 3.8), latitudinally-averaged for the Atlantic, and the satellite retrieved precipitation rate (Figure 3.9), referred to for the same climatological month of November? How are the data of sea surface temperature (Figure 3.4) useful to determine the wet deposition flux?

![Figure 3.8](image.png)

**Figure 3.8** Averaged latitudinal profiles of the atmospheric depositional fluxes for the Atlantic Ocean for Cl5DDs.

To answer this question it is important to take into account the parameterization of the wet deposition flux. The removal of semivolatile compounds by rain results from the scavenging both of gaseous dissolved compounds and particle-bound compounds. A common assumption is that the total wet deposition flux \( F_{WD} \) \([\text{ng m}^{-2} \text{s}^{-1}]\) is the product of the total (dissolved and particulate) concentration of contaminants in the rain \( C_R \) \([\text{ng m}^{-3}]\) and the precipitation rate \( p_0 \) \([\text{m s}^{-1}]\). Furthermore, since \( C_R \) is generally unknown, it is commonly expressed in terms of the concentration of contaminant in the aerosol \( C_{AER} \) \([\text{ng m}^{-3}]\) and the gaseous phases \( C_G \) \([\text{ng m}^{-3}]\):

\[
 F_{WD} = p_0 C_R = F_{WD, \text{Gaseous}} + F_{WD, \text{Particulate}} \\
 F_{WD, \text{Gaseous}} \approx \frac{C_G p_0 H}{RT} \\
 F_{WD, \text{Particulate}} \approx C_{AER} p_0 2.10^5 \tag{3.5}
\]

where \( R \) is the gas constant equal to 8.13 J/K mol, \( T[K] \) is the sea surface temperature, and \( H \) is Henry’s law constant [Pa m\(^3\)/mol], defined as the ratio between the compound’s saturated liquid vapour pressure and its solubility in water, and dependent on physicochemical properties and environmental data.
Q 2: Which are the main satellite images, already displayed in this case-study, that potentially affect the flux of air-water exchange? Also consider the global distribution of chlorophyll-α depicted in Figure 3.10.

Again, to answer this question, it is important to first examine the parameterization of this flux. The flux of gaseous contaminants between the atmosphere and the oceans is driven by a concentration difference and by the transport due to molecular and turbulent motion. This flux combines turbulent and molecular diffusion since it occurs through an interface, thus the parameterization is not straightforward. It is based in the classical two-layer stagnant boundary layer model, where it is assumed that a well-mixed atmosphere and a well-mixed surface ocean are separated by a stagnant film through which gas transport is controlled by molecular diffusion. The resulting net air-water exchange flux ($F_{AW}$ [ng m$^{-2}$ s$^{-1}$]) is a function of the air-water mass transfer coefficient $k_{AW}$, with velocity units (m s$^{-1}$), the POP dissolved concentration in the water ($C_{dis}^{W}$ [ng m$^{-3}$]) and the corresponding concentration in the gaseous phase in equilibrium ($C_{G}$ RT/H). This flux is, in fact, the net difference of two processes acting in parallel: absorption of gaseous POPs from the atmosphere to the water ($F_{AW,abs}$) and the volatilization of POPs from the water to the atmosphere ($F_{AW,vol}$).

$$F_{AW} = F_{AW,abs} - F_{AW,vol} = k_{AW} \left( \frac{C_{G}RT}{H} - C_{dis}^{W} \right)$$

(3.6)

where $H$ is, again, the Henry’s law constant and $k_{AW}$ the air-water mass transfer coefficient.
coefficient. $k_{AW}$ describes the rate at which chemicals partition between air and water surface and comprises resistance to mass transfer in both water ($k_W$ [m s$^{-1}$]) and air films ($k_A$ [m s$^{-1}$]):

$$\frac{1}{k_{AW}} = \frac{1}{k_W} + \frac{RT}{k_A}$$  \hspace{1cm} (3.7)$$

These mass transfer coefficients have been empirically defined based upon field studies using tracers such as CO$_2$, SF$_6$ and O$_2$. $k_W$ is calculated from the mass transfer coefficient of CO$_2$ in the water side ($k_{W,CO_2}$ [m s$^{-1}$]), itself generally correlated solely to wind speed ($u_{10}$, [m s$^{-1}$]) (Nightingale et al. 2009):

$$k_W = k_{W,CO_2} \left( \frac{Sc_{POP}}{600} \right)^{-0.5}$$  \hspace{1cm} (3.8)$$

$$k_{W,CO_2} = 0.24u_{10}^2 + 0.061u_{10}^2(1/100)(1/3600)$$  \hspace{1cm} (3.9)$$

where $Sc_{POP}$ [dimensionless] is the Schmidt number of the POP and 600 is the Schmidt number of CO$_2$ at 298K. Similarly $k_A$ can be estimated from the mass transfer coefficient of H$_2$O in the air side ($k_{A,H_2O}$ [m s$^{-1}$]), also generally parameterized as a function of the wind speed (Schwarzenbach et al. 2003):

$$k_A = k_{A,H_2O} \left( \frac{D_{POP,a}}{D_{H_2O,a}} \right)^{0.61}$$  \hspace{1cm} (3.10)$$

**Figure 3.10** Global distribution of the concentration of chlorophyll-\(a\) (chl-\(a\)) in the oceans in January (climatological monthly mean of 1998 - 2000).
where $D_{\text{POP},a}$ and $D_{\text{H}_2\text{O},a}$ [cm$^2$ s$^{-1}$] are the diffusivity coefficients of the POP and H$_2$O in air respectively.

Q 3: How can we determine the effect of short-term variations of the environmental data in the air-water POP fluxes if we use monthly means from satellite data?

3.5 Answers

A 1: Yes, we observe links between Figure 3.8 and Figure 3.9. In Figure 3.8 we observe an important variability in the Atlantic profiles of the fluxes, especially noteworthy for the wet deposition fluxes. Since the flux of wet deposition is directly proportional to the precipitation rate (see Equation 3.7), we can relate this variability to the spatial variability of the precipitation rates depicted in Figure 3.9. Therefore, it is clearly important to consider spatially-resolved data for the global assessment of POP cycling; in this context the use of remote sensing data is greatly justified. On the other hand, the wet deposition flux peaks in the high precipitation rates areas, such as in the Intertropical Convergence Zone (ITCZ). The positive gradient towards the northern hemisphere is related to the major emissions in the northern hemisphere.

As already pointed out in the demonstration section, the SST data will be useful to assess which fraction of contaminants partition to the gaseous phase and which fraction of the contaminants partition to the aerosol phase. By looking in detail at Equation 3.7 we see that the fraction of contaminants that are in the gaseous phase versus the ones in the aerosol phase relates to the relative importance of the wet-gaseous flux versus the wet-particle flux. The temperature will affect also the gaseous wet deposition flux through its effect on $H$ and also in the denominator of Equation 3.7. Putting it all together, the regions with lower SST, i.e. polar regions, will favour the particle-wet deposition.

A 2: The satellite-based remote sensing data that affect air-water exchange fluxes are sea surface temperature (Figure 3.4), wind speed (Figure 3.7) and chlorophyll-$a$ (Figure 3.10). From Equations 3.6, 3.9 and 3.11, it is clear that wind exerts an important effect on $k_{\text{AW}}$. On the other hand, temperature influences significantly the magnitude of $k_{\text{AW}}$ through its influence on diffusivities, Schmidt numbers and $H$. Temperature may affect the partition between aerosol and gaseous phases in the atmosphere and between dissolved and particulate phases in the water. On the other hand, since it has been proven that the particulate phase to which pollutants sorb is mainly phytoplankton, it can be foreseen that the amount of phytoplankton in the water column will modify the air-water exchange flux. This amount of phytoplankton is estimated from the satellite-derived chlorophyll-$a$ concentration.
A 3: It is important to account for the short-term variability of wind speed and precipitation in the depositional fluxes of POPs because it can potentially affect the monthly averages. Averages have been corrected by the appropriate parameter. If an oceanic Weibull distribution of wind speed is considered, then a shape parameter of 2 seems appropriate. Conversely, precipitation amounts can be modelled by an exponential distribution that depends on the average non-zero precipitation amount. More information can be found in Dachs et al. (2002) and Jurado et al. (2005).

3.6 References


3.6.1 Further reading
