

This idea has been applied recently by (Stroebe et al., 2006) to a multimedia model and for residence times in the atmosphere. Deviations for the Junge relationship when comparing to field data has been found for POPs that are associated to an important transport in water, and for substances with a strong tendency for revolatilization. According to this study, the Junge's variability relationship doesn't seem to be adequate to estimate the residence time, due to the important limitations found. However, their conclusions should be contrasted with a different model.

Under unsteady-state or dynamic conditions, a *characteristic time* is often calculated similarly as the mass divided by the output rate. It is the average time that the chemical spends in the compartment. *Half-life* ($t_{1/2}$) is defined as the time span within which the chemical decays by 50% of the initial concentration. This concept can only be used for a single compartment and assuming the loss by reaction as the main removal process, it can be derived from the residence time by $t_{1/2} = \ln 2 \tau$. However, if volatilization is important, the residence time and half-life are not directly related, since chemicals in addition to deposit can revolatilize, and this process may keep concentrations and thus it is possible that there is not a decrease in atmospheric concentrations with time.

LRAT can be deduced from a Lagrangian (moving parcel) or a Eulerian (box) model or using a flow equilibrium approach. The Eulerian approach, which pre-dates the Lagrangian model, is to treat the global environment as a series of connected multimedia environments, then calculate the spatial concentration distribution and express it as a distance within which most of the chemical resides. It is defined the *spatial range* as the distance within which the 95% of the substance is retained when the chemical is distributed at steady-state within the environment. In the Scheringer's 1-dimensional circilinear modeling approach (1996) (see Figure 6) the spatial range was defined as a dimensionless fraction of the Earth's circumference.

Using the Lagrangian approach, a *half-distance* was suggested by Van Pul et al. (1998) as the distance travelled at which half of the original chemical mass remains. Bennett et al. (1998) defined an analogous *characteristic travel distance (CTD)* at which $1/e$ remains, i.e. 37%. They showed that the CTD is given by the velocity of the mobile medium divided by an effective rate constant k_{eff} , which includes all exchange processes with, and degradation processes within, the other compartments. The half-distance is 0.693 times the CTD. Beyer et al. (2000) expanded on this and showed that k_{eff} is $(k_{\text{degr}} + k_{\text{D}}S)$ where k_{degr} is the reaction rate constant, k_{D} is the rate constant for transfer to other media (e.g. dry deposition velocity) and S is the "stickiness" of the receiving media, i.e. the fraction which is permanently retained. Beyer et al. (2000) also showed that the CTD under steady-state conditions is the product of the overall reaction residence time, the assumed velocity and the mass fraction in the mobile medium. The *equilibrium distance* is identical to the CTD (Hertwich et al., 1999). In addition, other new concepts for screening-level assessments of new contaminants are arising, such as the ratio persistence/LRAT classification (Klasmeier et al., 2006).

The key conclusion is that LRAT and persistence can be calculated and expressed in a variety of ways, nearly each of the different models of POPs found in the literature have developed an own way to estimate those parameters. Since a direct validation of those measures is not possible, conclusive results of model comparison studies are difficult and the validity of the values has been proven to depend on the configuration and context within is used the model (Fenner et al., 2005).

1.5 Transport and transformation processes of POPs

1.5.1 General characteristics of the transport and transformation processes

The spatial distribution of a chemical in environmental systems is essentially affected by transformation and transport processes. Transformation processes include processes that create a gain of mass of contaminant in the system (formation reactions, discharge of contaminant) and can be characterized by zero-order production rate J [$M L^{-3} T^{-1}$] and the processes that produce a lost in the system (degradation reactions) and are characterized by first order decay rate, k_R [T^{-1}]. The transport processes, move contaminants by means of random motion or directed motion. By means of simplicity the first type of transport processes are called diffusive and the second type advective processes, but it should be noted that diffusive processes include the so-called *diffusion* and the *dispersion* of contaminants and advective processes include the so-called *advection* and the transport associated for example to the deposition of particles. Additionally, under the diffusive transport one can distinguish the *molecular diffusion* from the *macroscopic turbulent diffusion*. One example of macroscopic turbulent diffusion, generally referred as *turbulence*, would be the flux of contaminants generated by the mixing of water.

Transport processes are evaluated numerically by means of fluxes [$M L^{-2} T^{-1}$] and their mathematical formulation differs between diffusive fluxes and advective fluxes. Diffusion is governed by Fick's First Law ($F_x = -D \partial C / \partial x$) and Fick's Second Law ($\partial C / \partial t = D(\partial^2 C / \partial x^2)$), where D [$L^2 T^{-1}$] is the molecular diffusivity. Advection flux is governed by the equation $F_x = v_x C$, where v_x [$L T^{-1}$] is the advective velocity. v_x and D generally depend on environmental properties, but on a molecular scale the molecular diffusion coefficient is a basic property of a chemical. The mathematical formulation of diffusion becomes more complex if the transport is occurring between two media, as it would be the case of the transport across an interface. This is due to the fact that transport by turbulence cannot cross an interface boundary, even though it can enhance it. In the boundary layers adjacent to the interface the transport occurs only by molecular processes. Indeed, the resultant flux will be a combination of molecular and turbulent diffusion. Among the different types of boundaries, the role of the air-sea interface should be stressed: it constitutes the primary entrance of contaminants to the oceans and accounts around the 70% of the Earth surface. Moreover, it has a vital role in the dynamic of contaminants and in the climate regulation.

Applying the mass balance principle, which has already been introduced earlier in 1.3 and which states that in every system mass must be conserved, the temporal change of the mass concentration (C [$M L^{-3}$]) is expressed as:

$$\frac{\partial C}{\partial t} = \left(\frac{\partial C}{\partial t} \right)_{\text{transport}} + \left(\frac{\partial C}{\partial t} \right)_{\text{transformation}} = D \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} - k_r C + J \quad [3]$$

The previous equation simplifies depending if the system is zero-dimensional, one-dimensional, steady state, etc. In the case of a one-dimensional system at steady state:

$$D \frac{d^2 C}{dx^2} - v_x \frac{dC}{dx} - k_r C + J = 0 \quad [4]$$

In the following sections are explained in detail the fluxes affecting in the air-sea transfer of POPs. Not only their parameterizations but also the major related unknowns. Afterwards is presented the molecular diffusive partitioning of contaminants between two phases, parameterized by means of partition coefficients. When equilibrium is achieved there is no tendency for net transfer of mass. Indeed, partition coefficients, are in fact a ratio of two concentrations at equilibrium.

1.5.2 Fluxes in the air-water-sediments system

1.5.2.1 Fluxes of POPs between the atmosphere and water

The following sketch presents the fluxes of POPs that occur through the air-water interface.

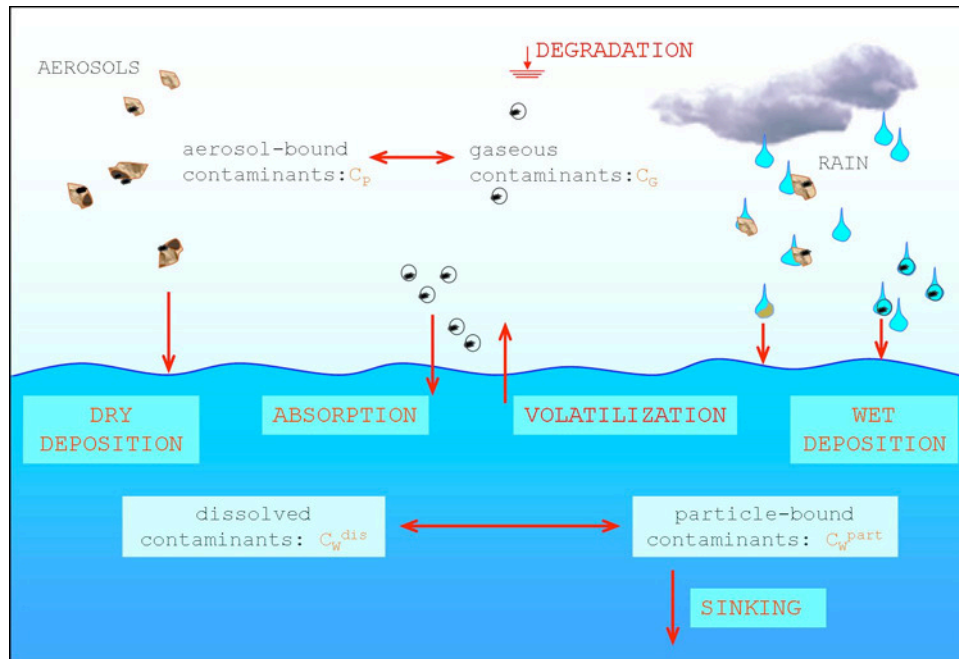


Figure 7 Fluxes of POPs between the atmosphere and the water

In the atmosphere, POPs partition between the aerosol and the gaseous phases and are subject to Long Range Atmospheric Transport (Bidleman, 1988). In the water, a common assumption is that they partition between dissolved and particle phases, but this simple partitioning may be extended to a third phase: the colloidal phase. Aerosol-bound contaminants may either deposit by gravity to the water surface (Dry deposition) or may be scavenged by falling raindrops (Wet particle deposition). Conversely, gaseous contaminants may diffuse to the water column (Absorption, Volatilization) or dissolve into the raindrops (Wet gaseous deposition). Additionally, fluxes like depletion of gaseous contaminants by OH radicals and marine spray may affect the amount of POPs in the atmosphere, although their extent is still not clear. By means of simplification it can be assumed that the major part of the marine spray re-deposits onto the water surface on short-mid-long term (Gong et al., 1997). On the other hand, snow scavenging or ice melting, may be determinant in high latitude water masses (Wania et al., 1999).

A common assumption is that the contaminants are well mixed within the atmospheric mixed layer (AML) and the oceanic mixed layer depth (MLD). The AML extends upward to the main atmospheric inversion and may be capped by a layer of shallow cumulus or stratocumulus clouds. A typical overall depth for the cloud topped marine boundary layer is approximately 1000 m. The MLD, the ocean region adjacent to the air-sea interface where temperature, salinity (and therefore the density) are fairly uniform due to the fact that is well mixed, is typically tend of meters deep.

The mixing of the MLD is primarily shear-driven, since the wind stress at the surface is the primary mixing agent, although significant convective mixing driven by the heat loss to the atmosphere takes place at night and during winter. Hence, MLD is major in winter and poorly stratified waters. On the other hand, the omission of the lateral advection of POPs is a common simplification in the open ocean, where the main entrance of pollutants is assumed to occur by the atmospheric deposition.

The relative importance of dry versus wet deposition processes has been notably debated. Measurements have shown that the importance of dry versus wet deposition varies considerably over time and space, and among chemicals. Furthermore, wet deposition fluxes themselves have been proven to be highly variable, both in sampling studies (Eisenreich et al., 1998) and in model intercomparisons (Rasch et al., 2000). Reports that compare the different atmospheric removal mechanisms for the atmosphere show that diffusive air-water exchange dominates over dry and wet deposition for POPs predominantly found in the gas phase, except in rainy regions, where wet fluxes become dominant, and close to urban areas with high concentration of aerosol particulate matter (Koester and Hites, 1992; Totten et al., 2001; Van Drooge et al., 2001; Tsapakis et al., 2006). Furthermore, dry aerosol and wet deposition is important for chemicals that have strong affinity to aerosols such as PAHs (Gevao et al., 1998) and for deposition of large particles (Holsen et al., 1993). However, the majority of those affirmations are based on measurements that have a short spatial and temporal extent. For this reason, a number of studies have intended to evaluate the dominance of one or the other flux for POPs on a global scale. The pioneering study of Duce et al. (1991) estimated a global major contribution of diffusive absorption over the oceans and for PCBs (65%), followed by wet deposition (44%) and by dry deposition (0.6%), using climatological data. There were, though, major uncertainties: he was relying on the product of a limited data set of concentrations and a number assumptions concerning washout ratios, deposition velocities, gas/particle distributions, Henry's law constants, considered fairly constant. By simple extrapolation, Baker and Hites (1999) also found global numbers of wet deposition fluxes about 3 times higher than dry deposition ones, referred to PCDD/Fs. By a totally different approach, chemistry transport models also present limitations when estimating the dominant flux. Indeed, even if hydrodynamic and atmospheric transport are modelled in detail, the corresponding parameterizations of the deposition fluxes are very simple and make use of single constant values (Shatalov et al., 2003). An interesting exception is the transport model TREND, applied to Europe and for PAHs (Van Jaarsveld et al., 1997); it was also found a major wet deposition fluxes. However, diffusive air-water exchange was surprisingly not taken into consideration for those contaminants.

Atmospheric-based fluxes do affect and are affected by internal water column fluxes. It has been proven that the diffusive air-water exchange may support or even control the concentrations found in phytoplankton in remote aquatic environments (Iwata et al., 1993; Dachs et al., 2002b). Dachs et al. (1999; 2002b) suggested that the occurrence of phytoplankton could reduce the dissolved

concentration of contaminants in sea-water, generating a major diffusive absorption to the ocean. What becomes an interesting question to evaluate these interplays in the global oceans, to solve how biomass scales relate to physical scales when estimating this flux at the global scale and how this could influence atmospheric residence times of POPs.

In summary, there are important gaps in the adequate parameterization of the spatial and temporal variability of deposition parameters affecting the fate of POPs. Due to the significant variability of the fluxes, especially in the wet deposition fluxes, it is important to estimate spatially resolved fluxes. Furthermore the dominant flux on a global scale is unknown and needs to account both dry, wet deposition and air-water exchange fluxes. These fluxes may have implication to water column, but the interplay between water-column fluxes with dry or wet deposition needs to be assessed. Indeed studies that analyze the interplay between air-water fluxes with water column fluxes are required, and this can be achieved through models that couple the processes occurring in both media.

1.5.2.1.1 Air-water exchange

The flux of gaseous contaminants between the atmosphere and the oceans is driven by a concentration difference and the transport by molecular and turbulent motion. Because of the lack of confidence of direct flux measurements, parameterization for air-sea gas exchange is based on indirect techniques, leading to the development of models combining sea surface measurements of concentration with parameterizations for the gas exchange rate (Watson and Upstill-Goddard, 1991; Wanninkhof and McGillis, 1999; Nightingale et al., 2000a). As pointed before, 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 from Liss and Slater 1974 where it is assumed that a well-mixed atmosphere and a well-mixed surface ocean are separated by a film on the liquid side of the air-water interface through which gas transport is controlled by molecular diffusion. The top of the stagnant film is assumed to have a concentration in equilibrium with the overlying air. The resulting net air-water exchange flux (F_{AW} [$\text{ng m}^{-2} \text{s}^{-1}$]) is function of a term with velocity units (the air-water mass transfer coefficient k_{AW} , [m s^{-1}]), the POP dissolved concentration (C_W^{dis} [ng m^{-3}]) and the corresponding concentration in the gaseous phase assuming equilibrium between both phases (C_G [$\text{ng m}^{-3}/H'$]). 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}).

$$F_{AW} = F_{AW_abs} - F_{AW_vol} = k_{AW} \left(\frac{C_G}{H'} - C_W^{\text{dis}} \right) \quad [5]$$

where H' is the dimensionless Henry's law constant ($H'=H/RT$), the Henry's law constant being the

equilibrium partitioning constant of the compound between air and water (see 1.5.3). The air-water mass transfer 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}]):

$$\frac{1}{k_{AW}} = \frac{1}{k_W} + \frac{1}{k_A H'} \quad [6]$$

These mass transfer coefficients have been empirically defined based upon field studies using tracers such as CO_2 , SF_6 and O_2 . Accordingly, a considerable effort has gone into determining an empirical relationship. Then, scaling to POPs is done by taking into account the different diffusivities and Schmidt numbers of the compounds. k_W is calculated from the mass transfer coefficient of CO_2 in the water side (k_{W,CO_2} , [m d^{-1}]), itself generally correlated solely to wind speed (u_{10} , [m s^{-1}]) (Wanninkhof and McGillis, 1999; Nightingale et al., 2000a; Nightingale et al., 2000b)

$$k_W = k_{W,\text{CO}_2} \left(\frac{\text{Sc}_{\text{POP}}}{600} \right)^{-0.5} \quad [7]$$

$$k_{W,\text{CO}_2} = 0.24 u_{10}^2 + 0.061 u_{10} \quad [8]$$

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_2O in the air side ($k_{A,\text{H}_2\text{O}}$ [m d^{-1}]), also generally parameterized function of the wind speed.

$$k_A = k_{A,\text{H}_2\text{O}} \left(\frac{D_{\text{POP},a}}{D_{\text{H}_2\text{O},a}} \right)^{0.61} \quad [9]$$

$$k_{A,\text{H}_2\text{O}} = 0.2 u_{10} + 0.3 \quad [10]$$

where $D_{\text{POP},a}$ and $D_{\text{H}_2\text{O},a}$ [$\text{cm}^2 \text{s}^{-1}$] are the diffusivity coefficients of the POP and H_2O in air respectively, defined elsewhere (Dachs et al., 2002b). Previous parameterizations have been applied in various studies (Totten et al., 2001; Dachs et al., 2002b; Gigliotti et al., 2002). From eq. 7-10 it is easily seen that wind exerts an important effect on k_{AW} . On the other hand, temperature influences significantly the magnitude of k_{AW} through its influence on diffusivities, Schmidt numbers and H' . Since wind speed and precipitation generally correspond to monthly averages, it is important to account additionally for the short-term variability and nonlinear influence of those parameters on the mass transfer coefficient. For example it is well-known that short periods of high wind speed account for most the time-integrated flux (Pérez et al., 2003). The nonlinear influence of wind speed

can be accounted by considering high resolution wind speed time series or average wind speed corrected by the appropriate parameter. If an oceanic Weibull distribution of wind speed is considered, then a shape parameter of 2 seems appropriate (Livingstone and Imboden, 1993) as also shown by Simó and Dachs (2002). Conversely, precipitation amounts can be modelled by an exponential distribution that depends on the average non-zero precipitation amount (Wilks and Wilby, 1999).

k_{AW} may be linked to major uncertainties, recently estimated in the range from 1% to 160% (Perlinger et al., 2005). It should be stressed that direct measurement of air-sea fluxes of gases is very difficult and they are often performed in idealised conditions of the laboratory. Besides the uncertainty in the Henry constant (Baker et al., 2004 rebuttal; Goss et al., 2004 correspondence), direct measurements of k_{WCO_2} show a broad scatter around the most widely used formulations which depend on wind speed alone. Those uncertainties are even higher for wind speeds larger than 15 m s^{-1} . Even if wind speed exhibits a major control on the surface turbulence, other parameters have seen to affect k_{WCO_2} and numerous studies are under this direction, such as dependence to microlayer surfactants, to rain rates, stratification, sea-ice (SOLAS, 2004). For example, rain has been identified as an additional parameter that enhances k_{WCO_2} values. This effect has been widely studied by Ho et al. (1997; 2004), who conclude that rainfall on the ocean significantly enhances the rate of air-sea gas exchange due to the turbulence generated by the impact of raindrops on the water surface. However its combined effect with other factors such as wind, etc is poorly known. On the other hand, it has been seen that other properties that characterize the degree of turbulence near the interface may be better suited for the parameterization of the gas-exchange rate other than wind speed (e.g. the ocean surface roughness and the mean square slope of short wind waves (Jähne, 2001)).

1.5.2.1.2 Dry deposition

Under the name of dry deposition flux (F_{DD} [$ng\ m^{-2}\ s^{-1}$]) it is accounted the deposition of aerosol-bound contaminants in the lack of precipitation. Even there are some techniques that allow direct measurements of dry deposition fluxes, there is a considerable uncertainty associated to them. Dry deposition is commonly reported as the product of the dry deposition velocity v_D [$m\ s^{-1}$] and air concentration of a pollutant in the particle phase C_P [$ng\ m^{-3}$] (Baker and Hites, 1999):

$$F_{DD} = v_D C_P \quad [11]$$

The tendency is to use a unique value of v_D in the open sea, around 0.1 $cm\ s^{-1}$. However, v_D greatly influenced by the aerosol size, by the atmospheric turbulent diffusion and by the atmospheric growth of particles at the high humidities. The corresponding parameterizations of v_D based on a model originally developed by Slinn and Slinn (1980) or improved variants (Williams, 1982), is

more than 20 years old, but are still widely used (Ondov et al., 1994; Nho-Kim et al., 2004). They show a minimum value of v_D for particles of approximately 0.1-1 μm diameter and for lower winds (Figure 8).

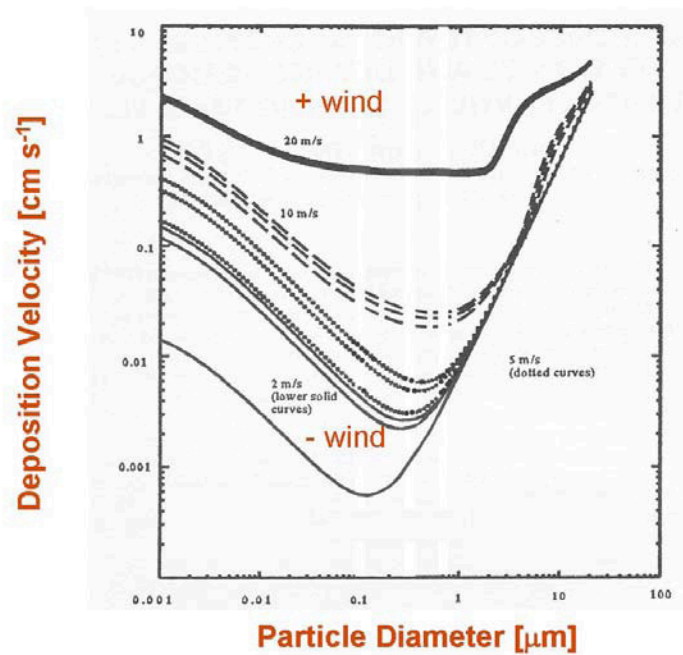


Figure 8 Dependence of dry deposition velocity on aerosol size, wind speed and atmospheric stability. the three curves plotted for each wind speed represent (from top to bottom) unstable, neutral and stable conditions (Williams, 1982).

When modelling the dry depositional flux of POPs, ideally, information on the particle size distribution of POPs should be combined with size-dependent deposition velocities (Holsen and Noll, 1992):

$$F_{DD} = \sum_i v_{D,i} C_{P,i} \quad [12]$$

Indeed the most reliable approach to estimate the dry deposition of POPs would require

measurements of size resolved aerosol composition (and inferred density), and the corresponding wind speed, temperature and relative humidity. Then the average dry velocity for each interval ($v_{D,i}$) would be estimated from models, using correlations as shown in Figure 8. However, this method is constrained to the fact that information on size distribution for POPs, i.e. the concentration of POPs in each aerosol size interval, other than for PAHs is extremely limited and essentially non-existent for the off-shore atmosphere. Research is then required to improve estimates of dry deposition velocity and as well to develop novel techniques for direct estimation of dry fluxes.

It is seen the importance of having a spatially resolved maps of sizes of aerosols. It can be done by MODIS sensor and by other new sensors that provide information of effective radius, the fraction of fine aerosol, etc. Dust, though, is generally underestimated and remote sensing supplies little information of the altitudes of dust plumes. Using such maps could be helpful to estimate the global dry deposition of POPs, but this has not yet been carried out until the present work was performed.

1.5.2.1.3 Wet deposition

POPs are scavenged from the atmosphere episodically by precipitation, both as gaseous contaminants which dissolve in the raindrops, and as particle-bound contaminants, which are incorporated in the rain within or below the clouds. Because of the complexity and amount of processes taking part, it is difficult to obtain a parameterization that covers all the related processes. A common assumption is that the dominant flux is the below-cloud scavenging (during the raindrop fall), discarding the contaminants captured during the in-cloud scavenging (the nucleation). It results a flux where the deposition of contaminants is the product of the dissolved and particulate concentration of contaminants in the rain (C_R [ng m^{-3}]) by the precipitation rate (p_0 [m s^{-1}]). Furthermore, since C_R is generally unknown it is common expressed in terms of the overall washout (W_T), which is the ratio of the concentration in rain and air measured simultaneously at ground level (Bidleman, 1988). W_T and the related gaseous and particle washouts have been explained in detail in section 1.5.3.3.

$$F_{WD} = p_0 C_R = p_0 W_T (C_P + C_G) \quad [13]$$

Uncertainty arises not only because this approach assumes a constant degree of equilibrium between the gas and water droplet, but also because there is no certainty that concentrations at the ground truly reflect concentrations in the cloud. In addition, the quantification of the amount of precipitation that falls is often uncertain and contrasts with the accuracy of the chemical composition measurements of precipitation. Island and coastal sampling locations frequently exhibit strong spatial gradients in wet deposition owing to local orographic and other perturbations (Van Drooge et al., 2001).

As occurring for dry deposition fluxes in marine atmospheres, the limited spatial and temporal extent of available wet deposition measurements coupled with large uncertainties in the magnitudes of the fluxes may constrain the reliability of existing estimations. Also it is required more accurate parameterizations of this flux in current models, which is generally formulated as a continuum process (Hertwich, 2001; Fenner et al., 2005). Indeed research is needed to develop global models that estimate wet deposition and also account for the frequency and intensity of the rain periods.

1.5.2.1.4 Sea-salt aerosol

The ocean emits a large amount of sea-salt aerosols, also termed marine aerosol, which are the result of the dehydration of sea-spray produced by bubble bursting. These sea-salt aerosols contain a substantial amount of organic material (Monahan and Dam, 2001; O'Dowd et al., 2004), indeed they provide a medium to which POPs attach due to their hydrophobic nature, specially to the organic fraction of sea-salt aerosol. The flux of sea-salt particles is thought to vary as the cube of the wind speed (O'Dowd and Smith, 1993) and its spatial distribution has been seen to be related to the optical signal from satellites (Kusmierczyk-Michulec and De Leeuw, 2002).

As stressed before, a main assumption is that the flux of POPs related to sea-salt aerosol is zero on a balance approach: all the POPs emitted by bubble bursting redeposits. But this simplification only applies on the long-term scale and the organic content of those marine aerosols could provide an additional deposition, which has not been estimated so far. Indeed, sea-salt aerosol could be an efficient scavenger close to the sea surface. There are currently large uncertainties in the production, residence times and removal of sea-salt (SOLAS, 2004). Direct measurements of fluxes of particles to or from the sea surface are not possible because there is sea spray production at the surface and as well deposition of particles of other origins, which current techniques cannot separate. In addition, besides the intense debate on the dependence of sea-salt on wind speed, there are a large number of ill-defined compounds in the sea surface organic microlayer (up to few hundred microns) that influence the composition of the sea-salt. An interesting work on the subject, is the one from García-Flor (2005), who found an enrichment of POPs in the sea-surface microlayer, which correlated to the organic matter.

1.5.2.1.5 Degradation in air

The process of POP degradation in the atmosphere is dominated by the reaction with hydroxyl radicals. This reaction is described by the equation of the first order:

$$\left. \frac{dC}{dt} \right|_{\text{degr,OH}} = -k_{\text{OH}} C_G C_{\text{OH}} \quad [14]$$

then the degradation flux, assuming that contaminants are well-mixed in the Atmospheric Boundary Layer (ABL), of height h :

$$F_{\text{degr,OH}} = h \cdot k_{\text{OH}} \cdot C_{\text{OH}} \cdot C_{\text{G}} \quad [15]$$

Where C_{OH} [molec cm⁻³] is the concentration of OH radical and k_{OH} [cm³ molec⁻¹ s⁻¹] is the degradation rate constant for air. C_{OH} varies substantially in the atmosphere and is strongly correlated to the intensity of sunlight, with night-time concentrations orders-of-magnitude lower than those observed during the day. Its distribution at a global scale has been reported in Spivakovsky et al. (2000), ranging between $23.4 \cdot 10^5$ molec cm⁻³ in the tropics and $0.9 \cdot 10^5$ molec cm⁻³ at the North Pole. Alternatively it is possible to use the following formula, where the hydroxyl concentration is directly related to temperature : $C_{\text{OH}} = (0.5 + 4 \cdot (T - 273.15)) \cdot 10^5$ (Beyer et al., 2003). On the other hand, temperature dependence of rate constant of the gas-phase reaction with OH-radical results in higher degradation in warmer periods.

Mandalakis et al. (2003) showed that gas phase concentrations of PCBs were depleted significantly due to the oxidative attack of OH radicals. Also, studies based on extrapolations of laboratory results to the global environment have hypothesized that reaction with OH is a dominant flux over water masses (Anderson and Hites, 1996). However they compared global estimations to a single global ocean deposition estimate from Duce et al. (1991) who had limitations as pointed in the beginning of this section (1.5.2.1). Analysis based on mass balance consideration in combination with field observations of PCB suggest that the OH reaction may be significantly overestimated (Axelman and Gustafsson, 2002). Furthermore, this dominance seems in contradiction with the diurnal cycle observed by Jaward et al. (2004) in pristine ocean atmosphere, where OH radical attack should be the main driver of the diurnal variations, but that measured cycles did not show this influence of OH radical. Indeed, surprisingly diurnal variations of POP concentrations showed maximums during the day. This could indicate that even degradation by OH attack may happen, other processes maybe driven by the marine carbon cycle could play a bigger role on POP short term dynamics. Jaward et al. (2004) suggested that there were a number of water column biogeophysical processes controlling the gas phase concentrations in the atmospheric boundary layer.

1.5.2.2 Fluxes of POPs in the water column

It has been demonstrated that water-column processes have a strong impact on the air-sea exchange of POPs (Dachs et al., 2000; Scheringer et al., 2004). Also atmospheric deposition may control the occurrence of POPs in planktonic webs, which are the first step for the introduction of POPs in the food web. Indeed it is important to develop models for water-column processes and their coupling with atmospheric processes. Furthermore, in coastal areas and shallow environments, sediments-

water exchanges play an important role. The following picture shows major processes affecting the fluxes of POPs in the water column and also the ones affecting the surface mixed sediments layer.

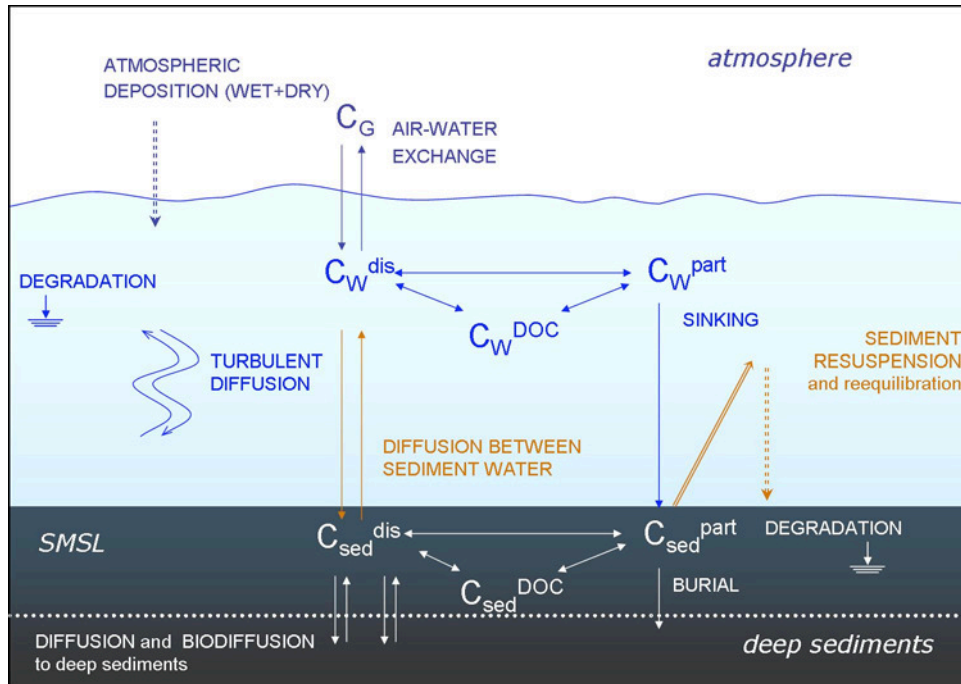


Figure 9 Fluxes of POPs in the water column and sediments

Namely, POP water column processes are (see Figure 9): partitioning onto colloidal and particulate matter with the sinking of particulate-bound contaminants, degradation of dissolved compounds, incorporation to trophic chains and transport of contaminants due mixing of water masses by turbulent diffusion and vertical advection. Additionally, in localized regions of deep water formation and down and up-welling regions advection vertical fluxes of POPs can be important, but its extent is poorly known. Also influence of mixing of waters masses by turbulent diffusion on POPs distribution is poorly known. The reason deals, a part from the complexity to model the highly variable turbulent fluxes, with the hypothesis that contaminants are assumed to be permanently well-mixed in the MLD, and no exchange of contaminants occur between the MLD and deeper waters.

The fate and transport of POPs in the water column is indeed largely controlled by their sorptive behaviour: POPs sorbed to particles, differently from the dissolved POPs, can be deposited by gravity; POPs sorbed to colloidal material can not sink, diminish the accumulation of contaminants to trophic chains and the fraction available for diffusive air-water exchange. Semi-empirical models

of equilibrium partitioning are used to determine the phase speciation of POPs and they are generally presented as having two or three components. In a two-component system, the sorbate (e.g. PCBs) is considered in either particulate or dissolved fraction, but this latter fraction may include both truly-dissolved POPs and POPs sorbed to colloids (dissolved organic matter DOC), especially in terms of the analytical procedures available. Three-component models treat the fraction sorbed to DOC as a separate phase. The three-phase representation has theoretical advantages for better characterizing the bioavailability and geochemical transport of POPs, but presents the practical difficulty of separating truly-dissolved sorbate from sorbate bound to DOC. The governing equations to characterize the proportion of POPs in each phase, assuming a three-phase representation:

$$\begin{aligned}
 C_W^T &= C_W^{\text{dis}} + C_W^{\text{DOC}} + C_W^{\text{part}} & [16] \\
 C_W^{\text{dis}} &= C_W^T / (1 + K_{\text{DOC}} \text{DOC} + K_d \text{TSM}) \\
 C_W^{\text{DOC}} &= C_W^{\text{dis}} K_{\text{DOC}} \text{DOC} \\
 C_W^{\text{part}} &= C_W^{\text{dis}} K_d \text{TSM}
 \end{aligned}$$

where C_W^{dis} [ng m^{-3}] is the truly-dissolved POP concentration, C_W^{DOC} [ng m^{-3}] the POP concentration sorbed to colloids, C_W^{part} [ng m^{-3}] is the POP concentration sorbed to suspended particles, DOC [ng m^{-3}] the concentration of colloidal organic carbon and TSM [ng m^{-3}] the concentration of total suspended particle matter, and K_{DOC} [$\text{m}^3 \text{ng}^{-1}$] and K_d [$\text{m}^3 \text{ng}^{-1}$] are the colloidal-water and solid-water equilibrium partition coefficients. Their exact parameterization is defined later, in the section dealing with partition coefficients (1.5.3).

Planktonic webs are the first step for the introduction of POPs in the food web, indeed they may be key in the transfer of pollutants to higher trophic levels. A general assumption is that the particulate phase to which pollutants sorb is mainly to phytoplankton. This affirmation is supported by studies where PCBs and PAHs follow the profile of the phytoplankton biomass (Dachs et al., 1997a; Dachs et al., 1997b). Besides, it has been demonstrated that POPs tend to sorb to phytoplankton rich in organic carbon (Swackhamer and Skoglund, 1991; Skoglund et al., 1996), which supports the idea that the cycling of POPs and the cycling of organic carbon are related. When phytoplankton sorption is dominant, parameterizations of K_d fail to quantify the particle-phase concentration, and the bioconcentration factor, which describes the partitioning between water and phytoplankton yields better results.

Even though the interactions between trophic status and pollutant fate have received some attention, the field is still far from being understood in a comprehensive manner (Berglund et al., 2001). The role of microorganisms (bacteria, virus, protozoa) in the fate of POPs is a subject which has been poorly studied. It should be highlighted the work of Wallberg et al. (2000; 2001), who proved that the communities dominated by heterotrophic organisms, i.e. bacteria, have a more efficient transfer of POPs to the higher levels of the food web and even higher bioaccumulation. Broman et al. (1996)

showed that particles of size 0.2-2 μm , i.e. basically bacteria, had POP concentrations at the same level or even greater than the bigger phytoplanktonic particles. This may also be sustained by the fact that bacteria sorb contaminants faster than phytoplankton, due to their lower volume to area ratio and their faster metabolism (Baker, 2002). Indeed in low productivity areas such as open ocean regions, bacteria may have an important role in the fate of POPs. Bacterial uptake could contribute, as phytoplankton does to enhance air-water exchange fluxes by uptake-driven depletion of dissolved POPs.

In addition, the level of contamination also may influence the primary production and indirectly the uptake of POPs by phytoplankton. According to the main hypothesis, when eutrophication occurs, the increased biomass and production in aquatic ecosystems cause a chain of events that results in reduced presence of POPs in phytoplankton. On the one hand, the corresponding increase of the sedimentation of organic matter causes an increasing downward flux of pollutants to the bottom. On the other hand the uptake of POPs in the fast growing phytoplankton is decreased as a result of “growth-dilution”, and lower amounts of pollutants are transported in the food-web (Larsson et al., 2000).

1.5.2.2.1 Sinking of particle bound contaminants

Sinking of particle-bound contaminants fluxes are usually parameterized as the product of the particle settling velocity (w_{se} [m s^{-1}]) and the particle-phase concentration:

$$F_{\text{SINK}} = w_{se} C_W^{\text{part}} \quad [17]$$

Sinking and export of POPs to the deep ocean has been described as a major removal mechanism from surface waters for the more hydrophobic POPs (Gustafsson et al., 1997a; Dachs et al., 2002b). However, such affirmation rely upon few and variable vertical flux measurements of POPs and on the simple parameterization presented in eq. 17, which masks a number of additional parameters controlling the fluxes. Variability of the particle settling velocity, dependent on the size of the particle and on the turbulent properties of the water masses, may affect the settling fluxes (Fasham, 2003). Nevertheless, it has not been demonstrated for POPs. An interesting study which supports this hypothesis found that in communities dominated by big phytoplankton sizes, sinking is of greater importance (Wallberg et al., 2001). Hence, the parameterization of the sinking flux presented previously should be developed in detail and coupled with suitable hydrodynamic (and ecological) models. On the other hand, since variability of sinking fluxes is significant, spatially resolved models are needed.

1.5.2.2.2 Degradation fluxes

The chemical and biological degradation of POPs F_{DEGR} [$\text{ng m}^{-2} \text{s}^{-1}$] in a square meter of water column of height h is given by:

$$F_{\text{DEGR}} = h k_{\text{dec}} C_{\text{W}}^{\text{dis}} \quad [18]$$

where k_{dec} [s^{-1}] is the degradation rate in the water column, higher for lower chlorinated PCBs. For PCBs it has been determined in Sinkkonen and Paasivirta (2000). Due to the extremely low degradation rates compared to the settling velocities of water column particles, this flux is generally considered not significant and not accounted in the majority of modelling exercises. However in cold oligotrophic lakes with long water residence times it has been demonstrated to be an important removal process for the less chlorinated compounds as shown in Diamond et al. (2005) for HCHs. Also, preliminary results show that PAHs may be affected by important biodegradation processes (Berrojalbiz et al., 2006), which is consistent with the extremely low fractions of collected sedimentary fluxes of PAHs respect to the total deposition fluxes (Tsapakis et al., 2006). Furthermore, in areas of very low settling velocities degradation could be locally a dominant flux. Nevertheless the dominance of the degradation fluxes in certain depths of the water column has not been studied to date.

1.5.2.2.3 Turbulent fluxes

By turbulent flux is understood as the flux of contaminants generated by eddy diffusion in the body of water. In short, turbulent flux is evaluated by the model through the Fick 1st and 2nd laws:

$$F_{\text{turb}} = \lambda \frac{dC}{dx} \quad [19]$$

$$\left. \frac{dC}{dt} \right|_{x=\text{cte}} = \left. \frac{dF_{\text{turb}}}{dx} \right|_{t=\text{cte}} \quad [20]$$

where λ ($\text{m}^2 \text{s}^{-1}$) is the turbulent diffusivity. Therefore the turbulent flux acts tending to eliminate the concentration gradients and it is composed by two fluxes acting in parallel and with opposite signs. The sense of the net flux goes from the higher to the lower concentration layer. This flux may be zero either in the absence of turbulence ($\lambda=0$) or if the concentration distribution is completely homogeneous ($dC/dx=0$).

The turbulent coupling of the oceanic mixed layer (MLD) with deep waters has proven to have implications in the cycling of nutrients. However the coupling of the oceanic MLD and deeper layers is not considered in terms of POPs transport. In open oceans POPs are assumed well mixed in the oceanic MLD and do not diffuse to deeper waters. This is a vast simplification since the upper

ocean is intermittently mixed and re-stratified through the combined effect of wind, surface buoyancy fluxes and penetrating radiation (Baumert et al., 2005). In this layer physical mixing combines with biogeochemical transformations which can modify exchanges with the atmosphere or export fluxes to the depth. Very few studies exist examining in depth the role of turbulent mixing in the fate of POPs, all dealing with the assessment of POPs in resuspended sediments enhanced in periods of high turbulence mixing and in costal areas (Ko et al., 2003; Hornbuckle et al., 2004). For other compounds such as CO₂, the role of turbulence has been examined with better detail and it has been observed important gradients of concentrations in the MLD (SOLAS, 2004), a different picture from what is generally assumed for POPs.

1.5.2.3 Fluxes of POPs between sediments and water

To model the transport of chemicals the sediments are separated between two layers; the surface mixed sediments layer (SMSL), a thin layer (around 1 cm) which is direct contact with the water column, and the deep sediments. Formulations for SMSL are described below.

The partition of chemicals onto the SMSL follow a similar 3-phase approach to the one presented for the water column, and with analogous partition coefficients: truly-dissolved in the interstitial water of the sediments (C_{sed}^{dis} [ng m⁻³]), sorbed to colloids in the interstitial water of sediments (C_{sed}^{DOC} [ng m⁻³]) and sorbed to sediment particles (C_{sed}^{part} [ng m⁻³):

$$\begin{aligned} C_{sed}^T &= C_{sed}^{dis} + C_{sed}^{DOC} + C_{sed}^{part} & [21] \\ C_{sed}^{dis} &= C_{sed}^T / (1 + K_{DOC, sed} DOC_{sed} + K_{d, sed} TSM_{sed}) \\ C_{sed}^{DOC} &= C_{sed}^{dis} K_{DOC, sed} DOC_{sed} \\ C_{sed}^{part} &= C_{sed}^{dis} K_{d, sed} TSM_{sed} \end{aligned}$$

Contaminants in sediments may be treated as diffusing through fluid-filled pores of a porous medium. The corresponding flux reduction is given by the porosity ϕ_{sed} , which is defined as the volume fraction of the pores. Besides the sinking flux, additional fluxes acting at the sediments-water interface are the resuspension flux and the water column-sediment's pore water diffusion flux (see Figure 9).

Marine sediments have been hypothesized to become a pool of contaminants available for mixing throughout the water column via resuspension, specially for coastal and shallow marine areas and during poorly stratified periods (Baker et al., 1991; Berglund et al., 2001; Bogdan et al., 2002; Ko et al., 2003). But their influence for deeper water columns is poorly understood. Also the driving mechanism in coastal areas between atmospheric based fluxes versus sediment-based fluxes is an interesting potential area of research, which has not yet been addressed.

1.5.2.3.1 Resuspension flux

F_{RES_sed} ($ng\ m^{-2}\ s^{-1}$) is the sediment resuspension flux. Additionally the desorption of contaminants from the resuspended sediments F_{RES_wat} ($ng\ m^{-2}\ s^{-1}$) is accounted. A possible parameterization is using μ_{res} [$ng\ m^{-2}\ s^{-1}$], the amount of particles per unit area and time that resuspend and which can be approximated by $\mu_{res} = 0.1\ z_{mix} TSM_{sed}$ ($1/(365*24*3600)$) (Schwarzenbach et al., 2003)

$$F_{RES_sed} = \mu_{res} C_{sed}^{part} / TSM_{sed} \quad [22]$$

$$F_{RES_wat} = \mu_{res} K_{d, sed} (C_W^{dis} + C_W^{DOC}) \quad [23]$$

where TSM_{sed} is the SMSL dry weight per volume and z_{mix} is its thickness.

1.5.2.3.2 Sediments-water diffusion flux

The sediment-water diffusion flux is composed by two fluxes acting in parallel: the diffusion from the interstitial water of the sediments to the water column (F_{WS_sed}) and the diffusion from the water column to the interstitial water of the sediments (F_{WS_wat}) (Schwarzenbach et al., 2003; Dueri et al., 2005):

$$F_{WS_sed} = k_{ws} (C_{sed}^{dis} + C_{sed}^{DOC}) \quad [24]$$

$$F_{WS_wat} = k_{ws} (C_W^{dis} + C_W^{DOC}) \phi_{sed} \quad [25]$$

where k_{ws} , [$m\ s^{-1}$] is the sediment-water diffusion coefficient and can be parameterized function of the molecular weight of the compound and the sediment's porosity (Di Toro et al., 1981).

1.5.3 Equilibrium partition coefficients

Partition coefficients are widely used in environmental models as has been shown before, and therefore some attention should be given to their parameterization. The concept of partition coefficients comes from the fugacity-based models, and thus this equilibration between two phases is due to diffusion. Once equilibrium between the two phases is achieved, there is no net transfer of mass between the phases and the relation of concentrations of chemical in each phase is constant and the resulting ratio is called equilibrium partition coefficient. Indeed the equilibrium partition coefficient $K_{i\ A,B}$ of a compound i between two phases, A and B is:

$$K_{i\ A,B} = \left(\frac{C_{i\ A}}{C_{i\ B}} \right)_{equil} \quad [26]$$

where C_{iA} is the concentration in the phase A and C_{iB} is the concentration in the phase B. Yet, in the real world there are many situations where equilibrium partitioning is not reached. Even in such cases, partitioning parameters are useful to characterize the equilibrium distributions would be given sufficient time or to determine the tendency of a chemical to accumulate in one compartment. On the other hand, equilibrium partition constants are needed for calculating the rate of transfer of a compound across interfaces, as shown before.

1.5.3.1 H, K_{OA} , K_{OW}

The partition coefficients between air and water (given by the Henry's Law constant H [$J\ mol^{-1}$], defined as well as the ratio between the compound's saturated liquid vapor pressure and its solubility in water), between water and octanol (K_{OW} []), and between air and octanol (analogous to the octanol-air partition coefficient K_{OA} []) characterize the equilibrium distribution of POPs between the different phases (Schwarzenbach et al., 2003) and where the octanol is a proxy for the organic matter. In short, K_{OW} would be a measure of the hydrophobicity of the compound and H a measure of the volatility. The equilibrium coefficients among the different phases are visualized in the following figure, where p_v is the saturated liquid vapor pressure (i.e. partitioning between air and the pure liquid phase of a compound), S_w are the solubility in water and S_o the solubility in octanol.

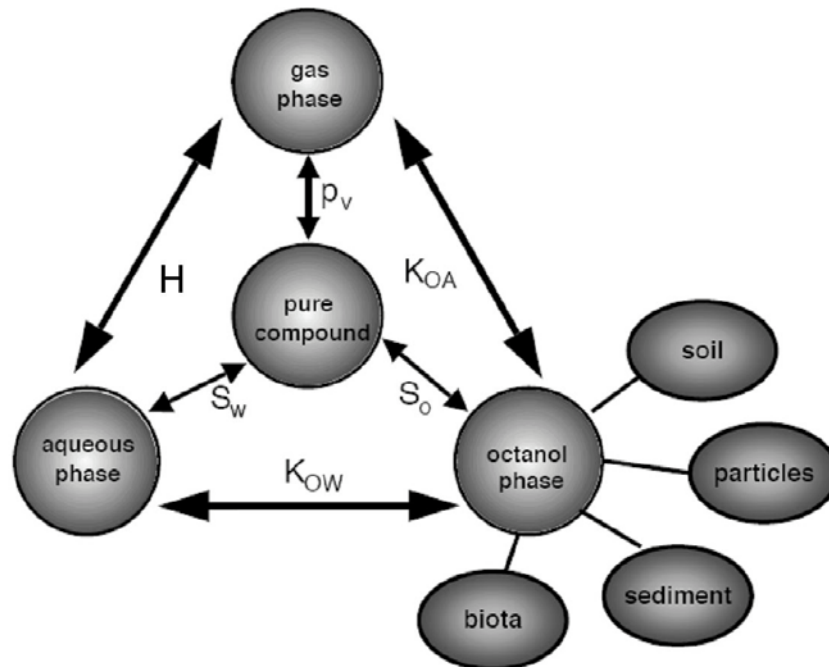


Figure 10 Partition coefficients among phases

The temperature has shown to be a critical factor in the partition of POPs between the various compartments. In general terms, as temperature decreases, vapour pressure decreases and sorption to organic matter is also greater. The variation of the partition coefficients with the temperature may be described in terms of thermodynamic or empirical relationships. On the other hand, as a general trend, the increase of molecular weight in POPs is associated to a decrease of solubility and vapor pressure. Thus the higher chlorinated POPs may have higher K_{OW} , higher K_{OA} and lower H . On the other hand, the PCBs have higher Henry's law constants than PCDD/Fs and PAHs (see Figure 11), indeed they may be found preferentially in the gas phase.

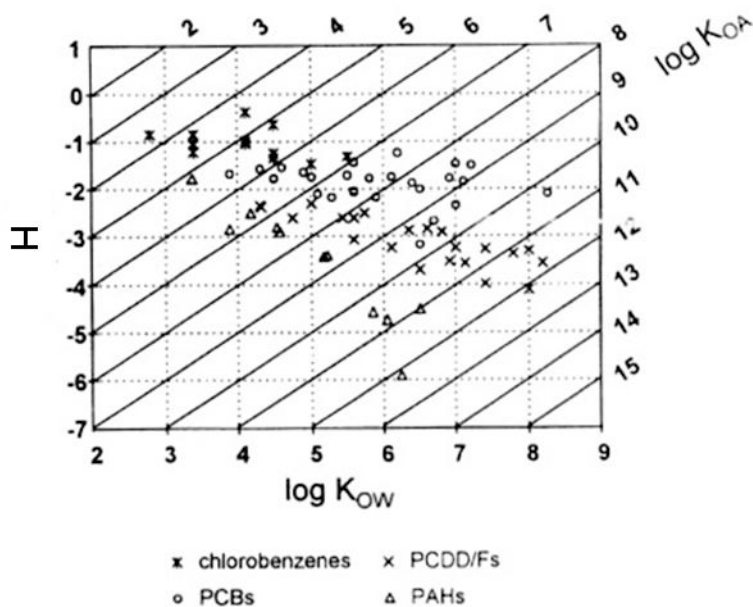


Figure 11 Chemical space of K_{OW} - H - K_{OA} for PCBs, PAHs, PCDD/Fs and chlorobenzenes

The determination of the Henry's law constant is subject to a heated debate (Baker et al., 2004; Goss et al., 2004). Furthermore, various sensitivity studies have noted that H among other parameters (k_{OC} , v_D , etc.), can constitute an important source of uncertainty when modelling the fate of POPs (Eisenberg et al., 1998b). This uncertainty should be in mind when evaluating the accuracy and reliability of multimedia POP models.

K_{OW} , H and K_{OA} cannot be measured in the reality, i.e. outside the laboratory, where POPs are sorbed to complex matrices. Next are described the equilibrium partition coefficients that are measured outdoors and that play a major role in air-water dynamics of POPs on a macromolecular scale.

1.5.3.2 Gas-particle partition coefficient K_p

A fundamental parameter for semivolatile compounds such as POPs is the equilibrium gas-particle partition coefficient (K_p [$m^3 \text{ ng}^{-1}$]), which allows to infer the gas-phase concentration from the aerosol-bound concentration (Pankow, 1994):

$$K_p = \frac{C_p}{C_G TSP} \quad [27]$$

where TSP [ng m^{-3}] is the total suspended particle matter in the atmosphere. Then the fraction of aerosol-bound POPs to total atmospheric POP (θ [0-1]) corresponds to:

$$\theta = \frac{C_p}{C_p + C_G} = \frac{K_p(TSP)}{1 + K_p(TSP)} \quad [28]$$

θ is favoured by the low temperatures and by higher concentrations of atmospheric particles. Furthermore, θ is greater for the less volatile POPs and for the compounds that sorb preferentially to soot such as aromatics. Early studies suggested relationships between $\log K_p$ and the logarithm of the subcooled liquid vapor pressure (Falconer and Bidleman, 1994) or the octanol-air partition coefficient (Pankow, 1994; Finizio et al., 1997). The gas-particle partitioning has been also described by means of adsorption onto soot carbon (Dachs and Eisenreich, 2000; Bucheli and Gustafsson, 2003). In this case, the K_p is driven not only by absorption into the organic matter (based on the octanol-air partition coefficient K_{OA}) but also by adsorption onto the soot phase (based on the soot/air partition coefficient K_{SA} [$\text{m}^3 \text{ng}^{-1}$]), with elemental carbon (EC) being a surrogate for soot:

$$K_p = f_{OM} \frac{\zeta_{OCT}}{\zeta_{OM}} \frac{MW_{OCT}}{MW_{OM} \times \rho_{OCT}} K_{OA} + f_{EC} \frac{a_{EC}}{a_{AC}} K_{SA} \quad [29]$$

where f_{OM} [0-1] and f_{EC} [0-1] are unitary mass fraction of organic matter and elemental carbon respectively in the atmospheric particles ($f_{OM} \cong 2 f_{OC}$ (Hedges et al., 2002)), ρ_{oct} the density of octanol, ζ activity coefficients, MW molecular masses and a surface areas. By means of simplification, it can be assumed a 15% of organic carbon and a ratio OC/EC=5 over the remote ocean, and that $MW_{OCT}/MW_{OM}=1$ $\zeta_{OCT}/\zeta_{OM}=1$. EC particles are ubiquitous in soils and sediments, often contributing to the 1 to 10% of the f_{OC} . Such particles exhibit a rather apolar and aromatic surface, consequently they exhibit a high affinity for planar aromatic compounds. Additionally, the temperature has a profound effect on the gas-particle partitioning of POPs in the atmosphere, so that lower temperatures shift the equilibrium from the gaseous to the particle phase.

K_p is an essential parameter to estimate the contribution of the gaseous and the aerosol-based deposition fluxes to the ocean. It is highly variable, a factor which promotes the evaluation of the fluxes with wide spatial coverage and accounting for the variability of environmental parameters that change K_p .

1.5.3.3 Overall scavenging ratio W_T

The scavenging ratio (W_T []) is the ratio of POP concentrations in rain and in the atmosphere (C_P+C_G). It is widely used for parameterization of wet deposition fluxes (1.5.2.1.3). This parameter is understood here as an equilibrium partition coefficient, it is assumed that equilibrium is attained rapidly between the chemical in the air and in the raindrop. It is expressed by means of a particle (W_P []) and a gaseous washout (W_G []) (Ligocki et al., 1985a; Ligocki et al., 1985b; Bidleman, 1988):

$$W_T = W_G(1-\theta) + W_P(\theta) \quad [30]$$

in which θ is the fraction of aerosol-bound POPs to total atmospheric POP concentration as defined in eq. 28. This definition has the condition that the chemical does not re-partition between dissolved and sorbed phase in the raindrop. Moreover, some attempts have found correlations between W_T and θ for PCBs (Van Ry et al., 2002) and PAHs (Franz and Eisenreich, 1998). However the application is site-specific and cannot lead to generalizations.

The W_G is the ratio of the rain-dissolved phase to gas-phase POP concentrations. Since it is assumed that equilibrium is attained rapidly between the gas phase and the dissolved phase in a raindrop, W_G is estimated as the inverse of the dimensionless Henry's law constant ($W_G=1/H'=H/RT$). However, field measured gaseous washouts of atmospheric POPs have found to be higher (Dickhut and Gustafson, 1995; Poster and Baker, 1996) and somehow dependent on the intensity of the rain (Koester and Hites, 1992). Simcik (2004) concluded that a better estimation of W_G is obtained when POP adsorption to the raindrop surface from the gas phase is considered. But this mechanism has not yet been accounted in multimedia models of POPs.

In contrast to gas scavenging, particle scavenging results not from equilibrium partitioning but rather from complex processes controlled by meteorological conditions, and physical-chemical properties of the aerosol. Thus W_P is often empirically determined. Reported average measured particle scavenging rates are highly variable and there's not an obvious dependence to the volatility the congener, particle diameter or rainfall intensity, despite the number of works dealing with the subject ((Mandalakis and Stephanou, 2004), see 3.2.3.3 for an extense revision) . An average value of 2×10^5 has been suggested in various transport POP models (Mackay et al., 1986).

1.5.3.4 Solid-water partition coefficient K_d

The solid-water equilibrium partition coefficient (K_d [$m^3 \text{ ng}^{-1}$]) is often employed to describe the

POP sorption to particles in the water column:

$$K_d = \frac{C_W^{\text{part}}}{C_W^{\text{dis-TSM}}} \quad [31]$$

Since the characteristic properties of most of POPs results in a good ability to associate to the various forms of particulate organic carbon (POC), K_d are generally expressed by means of organic carbon partition coefficients:

$$K_d = K_{OC} f_{OC} \quad [32]$$

where K_{OC} [$\text{m}^3 \text{ng}^{-1} \text{oc}$] is the particulate organic carbon partition coefficient and f_{OC} [0-1] is the unitary mass fraction of organic carbon in the water particles ($f_{OC} = \text{POC}/\text{TSM}$). For hydrophobic organic contaminants K_{OC} is considered to be a function of the octanol-water partition coefficient K_{OW} (Karickhoff, 1991). However relationships found in the literature, empirically determined, present a large variability, among other factors due to the narrow operational difference between POC and DOC. A major K_d than predicted by means of eq. 32 has been reported in marine sediments. In a similar way that adsorption to soot carbon in atmospheric particles affected K_p , the soot content of sediment particles (which can account for an important fraction, 12-31%) has been proved to increase K_d for PAHs (McGroody et al., 1996; Gustafsson et al., 1997b) and PCBs with planar-molecular structure (non-ortho) (Jonker and Koelmans, 2002; Bucheli and Gustafsson, 2003). Indeed it has been defined a soot-water partition coefficient (K_{WS}) (Walters and Luthy, 1984; Gustafsson et al., 1997b).

1.5.3.5 DOC-water partition coefficient K_{DOC}

The bioavailability and behaviour of hydrophobic organic chemicals are not only directly influenced by the particulate organic carbon (POC), as evaluated with the K_d , but also by the dissolved organic matter (DOC) present in the water column, sediment/soil porewaters (and groundwater). This DOC forms as colloidal-like medium but by means of simplification the interaction of organic pollutants with the Dissolved organic carbon (DOC) is envisaged primarily as a sorption process. Then, similar to the partitioning to POC, i.e. K_d , a DOC-water partitioning K_{DOC} [$\text{m}^3 \text{ng}^{-1} \text{oc}$] coefficient is defined:

$$K_{DOC} = \frac{C_W^{\text{DOC}}}{C_W^{\text{dis-DOC}}} \quad [33]$$

They have been correlated with $\log K_{OW}$, yielding in general a weak dependence for the water

column DOC, but a good dependence in the interstitial waters in sediments/soils (Baker et al., 1986; Burgess et al., 1996; Burkhard, 2000). It is substantial the variability of K_{DOC} , related ultimately in the operational definition of DOC (see Figure 12), which includes a wide range of structures and composition.

What should be retained for the modelling purposes is that a significant fraction of POPs sorb to DOC and it has an important effect in the dynamics of POPs. For example the sorption of DOC has been demonstrated to diminish the volatilization flux of PCBs about a 15%, with data based on field measurements (Totten et al., 2001). Microorganisms, through their efficient recycling of DOC, may also play an important role in the fate of POPs; but this has not yet been studied. Since an important number of POPs multimedia models do not account the 3-phase speciation (DOCs-dissolved-particle), the interpretation of their results should be considered with caution. Furthermore, this cautious look of model conclusions in the literature is also promoted by the uncertainty of the semi-empirical relations of the DOC-water partition coefficient found elsewhere.

1.5.3.6 Bioconcentration factor BCF

The bioconcentration factor (BCF [$\text{m}^3 \text{ng}^{-1}$]) is defined as the ratio of steady state concentration of the chemical in aquatic organism (C_{org} [ng ng^{-1}]) and the corresponding truly-dissolved chemical concentration in the surrounding water:

$$\text{BCF} = \frac{C_{\text{org}}}{C_{\text{W}}^{\text{dis}}} \quad [34]$$

BCF is appropriate when only passive diffusion processes are assumed to explain the uptake of contaminants by an organism, which would be the case for phytoplankton and bacteria. If ingestion also takes part, then the bioaccumulation factor (BAF) is used to describe the uptake of chemical. Since phytoplankton has been assumed to account for the total of organic matter in the water column, BCF is generally referred to units of organic matter mass and shall be expressed as $\text{BCF} = C_{\text{phyto}} / (C_{\text{W}}^{\text{dis}} \text{POM})$, where POM is the particulate organic matter concentration. POM itself can be assumed 1.8-2 times the particulate organic carbon (POC) (Hedges et al., 2002) and related to surface chlorophyll-a amount through the ratio of $0.003 \text{ ng}_{\text{chl}a} / \text{ng}_{\text{OC}}$ in the case of phytoplankton and bacteria (Jorgensen et al., 2000).

One of the most accepted methods to predict BCF values is correlating its logarithm to the octanol-water partition coefficient (Mackay and Fraser, 2000; Voutsas et al., 2002). However there are still some discrepancies about the lack of correlation between BCF and K_{OW} for the most hydrophobic POPs. Skoglund et al. (1996) attributed this lack of correlation to kinetic limitations. Del Vento and Dachs (2002) additionally attributed it to low permeability of cellular membranes to large

molecules.

During periods of fast-growing algae, as an example, the equilibrium partitioning between the phytoplankton and its surroundings may not be achieved. Instead, the accumulation of the chemical may depend on several processes occurring at the same time (uptake, depuration, growth...) (Skoglund et al., 1996; Axelman et al., 1997; Jeremiason et al., 1999; Baker, 2002). The bioconcentration factor (BCF) is then determined using a mechanistic mass balance, where the various uptake and loss processes are evaluated and assuming steady-state. The simplest approach is to treat the organism as one compartment and draw a mass balance envelope around the organism. The time-dependent accumulation of a chemical in phytoplankton or bacteria is given by:

$$\frac{dC_{\text{phyto}}}{dt} = k_{\text{uptake}}C_{\text{W}}^{\text{dis}} - (k_{\text{depuration}} + k_{\text{growth}})C_{\text{phyto}} \quad [35]$$

where k are first order rate constants of the different processes. Then at steady state ($dC_{\text{phyto}}/dt=0$) the BCF is given by:

$$\text{BCF}^{\infty} = C_{\text{phyto}}^{\infty} / C_{\text{W}}^{\infty \text{dis}} = k_{\text{uptake}} / (k_{\text{depuration}} + k_{\text{growth}}) \quad [36]$$

A more complex approach would treat the surface and matrix of organism as two separate compartments (Del Vento and Dachs, 2002), where there is first fast adsorption to the phytoplankton surface followed by diffusion into the matrix in a partitioning like mechanism. While for phytoplankton, absorption may dominate the total bioaccumulation potential (Skoglund et al., 1996), the smaller size of bacteria and their higher specific surface area suggest that bacterial uptake may be dominated by surface adsorption (Axelman et al., 1997; Sobek et al., 2006). Several studies have focused during the last decade on the experimental determination of uptake and depuration constants (Jorgensen et al., 2000). However, it should be noted the lack of experimental uptake and depuration rate constants of POPs by bacteria, which complicates the modelling of the uptake of chemical by phytoplankton or bacteria.

1.6 POPs and the carbon cycle

Among the sorbents present in the environment, organic matter has been proven to play an essential role in the overall sorption of POPs. It has been clearly seen when a large number of equilibrium partition constants with the solid or colloidal-medium phases have found to correlate with the octanol-water partition coefficient K_{OW} , where octanol is a surrogate of organic matter. The dynamics of POPs are therefore linked intimately to the carbon cycle.

The organic carbon in the sea is traditionally subdivided between the dissolved organic carbon (DOC), defined operationally as the organic material that passes a filter of pore sizes near 0.4-0.7 μm , and the particulate organic carbon (POC) (Valiela, 1995). However, such dichotomy is artificial and in reality there is a continuum (see Figure 12). Furthermore, DOC comprises a colloidal fraction (COC) and truly-dissolved fraction (DOC_{dis}), $\text{DOC} = \text{COC} + \text{DOC}_{\text{dis}}$. COC and POC retain persistent organic contaminants and the knowledge of their dynamic gives hints on POP modelling in the water column.

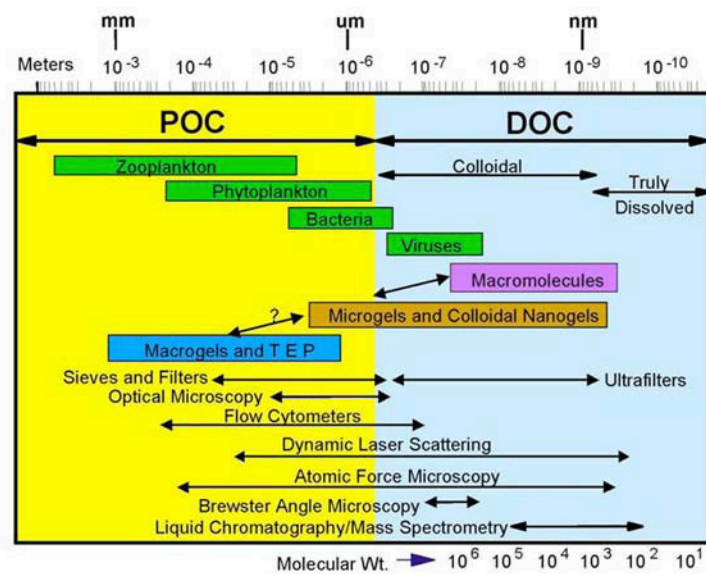


Figure 12 Characterization of DOC/POC in the water column (adapted from Lalli and Parsons, 1997)

DOC represents around the 97 % of the total organic carbon (Murray, 1992), and among DOC the 10-47% is COC (Gustafsson et al., 2001). DOC includes a wide range of constituents from truly dissolved small molecules like acetate to macromolecules such as humic acids, to filter-passing

submicro-meter-sized particles such as viruses. Essentially it can be assumed that DOC can either be formed in situ (*e.g.*, by solubilizing particles, through zooplankton excretion, by degradation of organic matter by bacteria), or transported through mixing of waters or by excretion of vertically migrating zooplankton. Even though, the relative contributions of these mechanisms remains unclear and the picture presented before is even more complex. Hence, DOC is consumed by heterotrophic bacteria, being responsible to the fact that a substantial amount of fixed carbon passes through the microorganisms, especially in tropical and temperate waters (Lalli and Parsons, 1997; Azam, 1998). Nevertheless, there is still limited knowledge on whether and how eutrophication processes affect DOC and the colloidal fraction in water. What should be kept in mind when modelling the transport of POPs is that DOC doesn't settle but forms a particle-like medium with a non negligible sorbing capacity.

Much of the particulate organic carbon (POC) is biogenic of recent origin, consisting of planktonic algae, bacteria and detritus. It comprises "dead" and "alive" material. Particulate material is processed by both microbial and zooplankton communities. It can be exported vertically from the euphotic zone by gravitational deposition, physical mixing of water masses and active transport by vertically migrating organisms. The first mechanism has been the most studied in the models of export of organic carbon. This is why sinking fluxes of POPs are mostly modelled as bounded to particles depositing by gravity. Mixing by turbulent diffusion, which also affects DOC, is especially important in the Mixed Layer Depth and has important seasonal changes, but the exact extent to which turbulence affects DOC is still uncertain (Burd et al., 2002), and nothing has been said on its influence on POPs cycling. Lateral advection and advective inputs from resuspended sediments constitute a significant source of organic carbon to the deep waters, as has been proven in the eastern Alboran Sea (Sanchez-Vidal et al., 2005). Concerning the active transport by vertically migrating organisms research has been mainly focused to diurnal migration by zooplankton. However, these are only sufficient to transport material 200-300 meters. Even so, this would potentially take that material out of the euphotic zone and prevent further processing of it in the upper water column. The only "back of envelope" estimation of the magnitude of active transport of POPs by zooplankton is that reported by Jaward et al. (2004).

With the deployment of sediment traps it has been seen that particle flux within the oceans does, for the most part, decrease with depth (Fasham, 2003). Traditionally, the change of particle flux with depth has been depicted using power-law relationships $F(z)=az^{-b}$, where the constants a and b are determined empirically. Accordingly, Baines et al. (1994) proposed the following parameterisation for the organic carbon flux collected at 200 m depth versus the surface concentration of chlorophyll a (chl_a [$mg\ m^{-3}$]) and for the oceans:

$$F_{OC}=(10^{(2.09+0.81 \log chl_a)}) (10^6/24*3600)$$

[37]

However, a single relationship cannot accurately describe changes in particle flux with depth globally. Furthermore, the fluxes between 100 and 1000m (twilight zone) are not well understood and are very variable. Part of this variability and decrease is explained by physical processes (aggregation/desaggregation, water masses diffusion or advection) and by biological processes (variations in mesopelagic communities, vertically migrating zooplankton).

The processing of DOC and POC by the different trophic levels is essential to describe the carbon cycle:

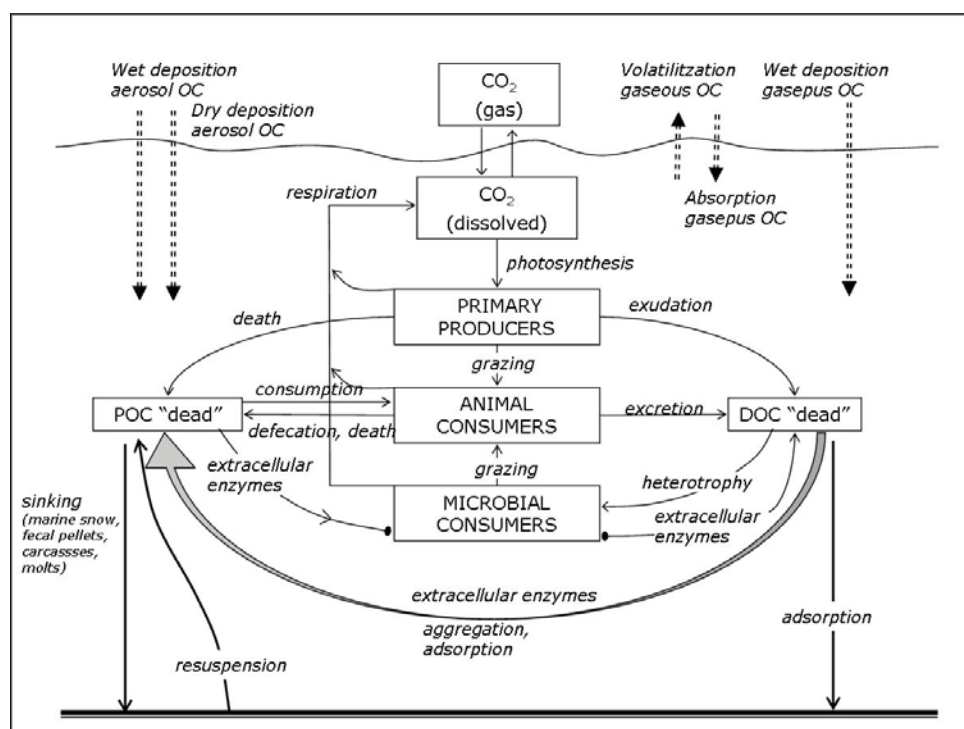


Figure 13 The Carbon Cycle (adapted and modified from Valiela 1995)

Arrows represent processes and boxes, the “deposits” of organic carbon. It has been distinguished the POC/DOC that constitutes an alive organism from the “dead” POC/DOC (dead organisms, detritus, aggregations). This cycle is in fact an adaptation from Valiela (1995) where it has been stressed the role of heterotrophic bacteria as DOC consumers and the introduction of organic carbon by dry, wet and air-water exchange has been also considered for reasons given below.

The marine carbon cycle is even more complex than the presented in Figure 13; vertical transport