Sources, Transport and Fate of Organic Pollutants in the Oceanic Environment

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Chapter 8
Sources, Transport and Fate of Organic Pollutants in the Oceanic Environment

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8.1 Introductory Remarks

Industrial, agricultural and other anthropogenic activities have lead to the introduction of thousands of pollutants, most of them synthetic organic compounds to the marine environment (Dachs and Méjanelle 2010). A fraction of these organic compounds, called persistent organic pollutants (POPs), are chemicals that have become a major concern because of their toxicity, persistence, bioaccumulation tendency, and susceptibility to undergo long-range atmospheric transport. Traditionally, much attention have been given to a few families of POPs, such as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) such as DDT and hexachlorobenzene (HCB) and other byproducts of industrial processes or combustion such as dioxins and furans (PCDD/Fs) and polynuclear aromatic hydrocarbons (PAHs). However, these chemicals are a small fraction of the total known pollutants in the marine environment (Dachs and Méjanelle 2010) and presumably of the total potential pollutants occurring in the environment (Muir and Howard 2006). In any case, these few families of POPs have been detected everywhere on earth in abiotic and biotic matrices (Gioia et al. 2006, 2008a; Gilman et al. 1997; Jaward et al. 2004). Today, compounds with similar or different physical chemical properties (such as the polybrominated diphenyl ethers, PBDE and other fluorinated compounds, PFs) are being manufactured and widely used,

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potentially entering the environment and providing new challenges for the maintenance of its quality. Our current knowledge indicates that the cycling of these chemicals in the environment is highly complex; indeed their local, regional and global cycle is controlled by repeated air-surface exchange and interactions with the carbon cycle, especially the organic and soot carbon fractions. Because, a fraction of these chemicals are hydrophobic, they have the potential to accumulate in all the trophic levels of ecosystems, including those far away from sources. The number of known organic pollutants in marine waters, and other environmental compartments, has increased dramatically during the last decade, in part due to important analytical developments. Nowadays, even though much of our knowledge on organic pollutants is centered on a few chemical families (PCBs, HCHs, DDT, PAHs, etc.), these families should be viewed as markers or “surrogates” of other pollutants in marine waters with similar physical–chemical properties. In addition, other chemicals with different physical–chemical properties (i.e., greater water solubility, low volatility) may reach coastal and open oceans via rivers and undergo different environmental behavior, due to their ionic character. In fact, some of newly emerging compounds have been suggested to behave as passive tracers in waters (Yamashita et al. 2008), a behavior quite different from that shown by legacy POPs such as PCBs or HCHs.

8.2 The Anthropogenic Organic Chemosphere in the Marine Environment

There are large numbers of anthropogenic organic substances in the marine environments at trace levels. Crutzen and Stoermer (2000) has introduced the term “anthropocene” for the recent last two centuries emphasizing the role of humans as a major driving geophysical force of the earth system. Steffen et al. (2007) have explored the evolution of the anthropocene, and have suggested two stages, the first being the industrial era from 1800 to 1945 and the second being the great acceleration from 1945 up to present. The number of synthetic organic substances used by humankind has increased enormously during the second half of the twentieth century, even though some substances such as PCBs, started their production during the 1920s. Obviously, chemical pollution due to hydrocarbons such as PAHs or alkanes must have started to increase during the industrial era, and even before owing to the use of fossil fuels. We can hypothesize that the second stage or great acceleration (from 1945) has represented an explosion in the introduction of chemicals to the environment, resulting in an increasing pressure to ecosystems and humans. Some chemicals, such as PAHs, have been in the environment since the initial stages of humankind due to forest fires and use of wood as an energy source. However, there are thousands of chemicals that have been introduced to the environment for the first time during the last decades and evolution has not have the opportunity to work out the mechanism to deal with them, leading in some cases to adverse effects in ecosystems and humans. The presence of synthetic organic substances in the environment can be viewed as a “new” driver that has appeared in the anthropocene. Its importance may not be linked to the occurrence of a given pollutant, or a small group of them, but by the fact that the total number of pollutants in any coastal ecosystems may be huge. A fraction of these pollutants are persistent, thus they could stay in the marine environment for decades or hundreds of years. As the use of chemicals change due to progress in industrial/agricultural applications and due to new regulatory limitations, then new chemicals are introduced in marine regions. The modification of the composition of the biosphere, in coastal and open ocean ecosystems, can be viewed as another vector of global change, one that is closely interrelated with the other vectors of global change such as social/economic changes, climate change, loss of biodiversity and perturbations in the hydrological cycle.

Since the 1970s, there has been an increasingly wider scientific field dealing with environmental risks associated with the occurrence and fate of POPs. Fifty years after the initial awareness of the potential hazard represented by synthetic chemicals, the study of the sources, transport, fate and impact on ecosystems and humans has became a major scientific field which has matured in many aspects, and has had an important impact on international legislation: for example the United Nations’ Stockholm convention on POPs (UNEP 2001), the UNECE protocol (UNECE 1998), and European Union REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) Directive. However, the field is still in its infancy in terms of being able to evaluate the total contamination present in ecosystems (or humans) and the real impact that this contamination, made up by thousands of chemicals, has on individuals and ecosystems.

The chemicals introduced are numerous and come from many different applications ranging from agricultural herbicides, pharmaceuticals, detergents, flame retardants, di-electric fluids, combustion by-products and numerous other applications (Muir and Howard 2006; Schwarzenbach et al. 2003). Table 8.1 presents a list of most non-volatile organic chemicals that have been described in coastal or open ocean waters. Chemicals are classified by families and in many cases one of these families contains tens or hundreds of different compounds (for example PAHs, PCBs, etc.). The list would be larger if pollutants that have been reported in other environmental compartments such as soil, atmosphere or freshwater, had been included (see for example Kasprzyk-Hordern et al. 2008). Table 8.1 does not contain degradation products of known pollutants (Farré et al. 2008) which can be toxic as well and induce adverse effects in organisms. Usually, these degradation products are more polar than parent compounds. A few tens of these chemicals are currently regulated by various international/national laws, but many are not yet regulated. In fact, there are contradictory situations where some chemicals are of illegal use, such as cocaine and other illicit drugs, but their occurrence in continental waters is generalized and not regulated (Postigo et al. 2009).

So far no study has reported all the compounds listed in Table 8.1 in a single environment or a significant fraction of them. This is because of the analytical challenge of analyzing, detecting and characterizing all pollutants. Even for fossil-fuel residues found in the environment, the chemical structure of some fractions

Table 8.1 Non-volatile organic chemicals reported in transitional and coastal waters (Dachs and Méjanelle 2010)

Chemical family	Historical or current use application
Polychlorinated biphenyls (PCBs)	Industrial, various
DDTs (1,1,1-trichloro-2,2-bis(4-chlorophenyl) ethane)	Insecticide
Hexachlorbenzene (HCB)	Insecticide
Aldrin	Insecticide
Dieldrin	Insecticide
Endrin	Insecticide
Toxaphene (polychlorinated bornanes)	Insecticide
Chlordane	Insecticide
Heptachlor	Insecticide
Polychorinated dibenzodioxins and furans (PCDD/Fs)	Combustion byproduct
Hexachlorocyclohexanes (HCHs)	Herbicide
Polycyclic aromatic hydrocarbons (PAHs)	Combustion byproduct, fossil fuels
Polybrominated biphenyl ethers (PBDEs)	Flame retardant
Hexabromocyclododecane	Flame retardant
Nnonylphenol polyethoxylates (NPEO)	Surfactant
Nonylphenols (NP)	Degradation product of NPEO
Octylphenols (OP)	Degradation product of NPEO
Bisphenol A	Plasticizer, antioxidant
Phthalates (phtalate esters)	Plasticizer
Alkanes and other hydrocarbons	Fossil fuel, combustion byproduct
Non resolved hydrocarbons (UCM)	Fossil fuel
Chlorinated alkanes	Industrial (lubricants, flame retardants, etc.)
Organotins (Tributiltin, triphenyltin, etc.)	Antifouling agent
Atrazine	Herbicide
Simazyne	Herbicide
Diuron	Herbicide
Hexazinone	Herbicide
Endosulfan	Pesticide (insecticide/acaricide)
Linear alkylbenzene sulphonates (LAS)	Surfactant
Linear alkylbenzenes	Byproduct of LAS
Bis(4-chlorophenyl) sulphone	Plasticizer, byproduct of pesticide synthesis
Glyphosate	Herbicide
Irgarol	Antifouling agent
Methyl tertiary-butyl ether (MTBE)	Gasoline additive
Benzotriazoles	UV stabilizers, pharmaceuticals and others
Trialkylamines (TAM)	Surfactant byproduct
2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB)	Flame retardant
Bis-(2-ethylhexyl)-tetrabromophthalate (TBPH)	Flame retardant
Perfluorinated compounds (PFOS, PFOA and others)	Industrial and other
Polychloronaftalenes	Industrial and other
Drugs of abuse (cocaine, etc.)	Illicit drugs
Pharmaceuticals (various)	Pharmaceuticals
Veterinary antibiotics	Antibiotics
Musk fragances	Fragrances, day care products

(*continued*)

Table 8.1 (continued)

Chemical family	Historical or current use application
Sucralose	Sweetener
Estrone	Natural estrogen, pharmaceutical
17β-estradiol	Natural estrogen, pharmaceutical
17α-ethynylestradiol	Pharmaceutical

remains largely uncharacterized (Rowland et al. 2001; Donkin et al. 2003; Melbye et al. 2009). Furthermore, the list of chemicals present in the environment must be several orders of magnitude longer than those ever reported, since tens of thousands of organic chemicals have been used by humankind. Due to the lack of appropriate analytical methods to survey such a large number of compounds at trace levels, an unknown number of chemicals have already being introduced in the environment and have not yet been reported in the literature. A crucial characteristic of the environmental burden in organic pollutants is that their total amount in the environment is unknown. Oceans will often be the ultimate receiving compartment for such substances.

8.3 How Do Organic Pollutants Reach the Ocean? Atmospheric and River Inputs

The oceans cover 70% of the ocean surface and have important reservoirs of organic carbon (preferred sorbing phase for many POPs). Therefore, the oceans play an important role in controlling the environmental transport, fate and sinks of POPs at regional and global scales (Wania and Mackay 1996; Dachs et al. 2002). Although POP concentrations in the open ocean have been shown to be lower than those observed in coastal areas (Iwata et al. 1993; Dachs et al. 1997a), the large oceanic volume implies that they may represent an important inventory of POPs (Jurado et al. 2004). Traditionally, research on oceanic organic pollutants has been centered in hydrophobic, persistent and semivolatile pollutants, indeed POPs. Lately, other families of organic pollutants such as perfluorinated compounds have received an increasing attention (Jahnke et al. 2007). For those chemicals that can undergo atmospheric transport due to their semi-volatility as all legacy POPs, the pathway atmospheric transport – deposition – and incorporation to plankton and transfer through the food web is of key importance for understanding their fate and transport. For other ionic chemicals, or non-ionic but limited volatility, their distribution in the ocean will be dominated by water transport, even though they can also be subject to bioaccumulation processes. The fate and transport of these ionic and/or low volatility chemicals is much less understood than that of legacy POPs, but for these chemicals the atmosphere will play a negligible or small role as a source, and their inputs in the marine environment will be dominated by riverine inputs (Pistochi and Loos 2009). Even for legacy POPs, rivers can be significant sources of POPs to the coastal environment (Gomez-Gutierrez et al. 2006; Zhulidov et al. 2000), even though, it is commonly accepted that atmosphere dominates inputs to the open ocean.

The atmosphere has been regarded as the most important and rapid route of transport for POPs to surface waters. POPs partition between gas and aerosol phases and may then be removed from the atmosphere by four major mechanisms: dry deposition of particle bound pollutants, diffusive gas exchange between the atmosphere and the surface ocean, scavenging by rain (wet deposition) and OH radical degradation. Figure 8.1 is a conceptual diagram of the major processes affecting POPs in the oceanic atmosphere. Many studies have acknowledged the importance of air–water exchange in understanding the environmental fate of POPs at local, regional and global scales (Hornbuckle et al. 1995; Nelson et al. 1998; Totten et al. 2004; Rowe et al. 2007; Gioia et al. 2008a, b; Nizzetto et al. 2008). Gaseous exchange of contaminants between the atmosphere and the ocean is driven by a concentration difference and transport by molecular and turbulent motion. Air–water gas exchange is the most dominant depositional process at the global scale compared to wet and dry deposition (Jurado et al. 2004) for those POPs which atmospheric occurrence is mainly in the gas phase (PCBs, HCHs, lighter PAHs). Conversely, for some PAH and PCDD/F, which due to their planar structure have higher affinity to aerosol soot carbon (Dachs et al. 2000; Lohmann et al. 2007), dry/wet deposition can play an important role (Jurado et al. 2005). Available measurements of POP air–water exchange fluxes in remote oceanic regions are very scarce due to the difficulties associated with the sampling procedures for POPs (e.g., large volume, partition to colloids, etc.), shipboard and laboratory contamination and the costs associated with the use of ships in the open ocean. This is

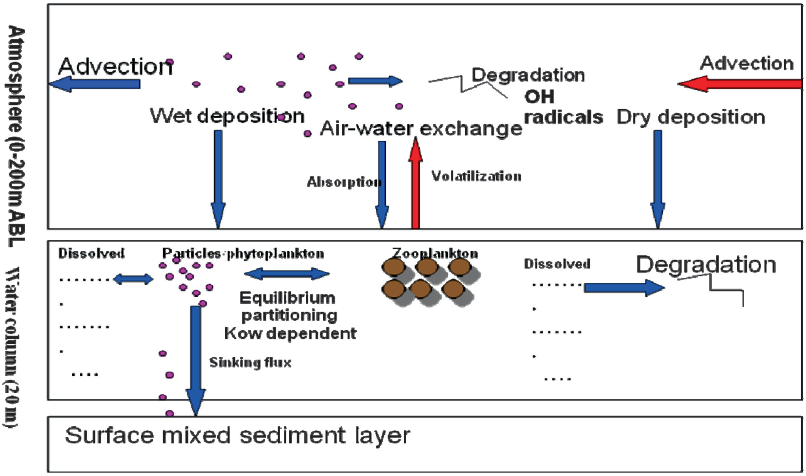

Fig. 8.1 Major processes affecting POPs in the atmosphere and the ocean

because of the inherent difficulties and very demanding sampling and analytical requirements for these compounds at ultra-trace levels which limits realistic data to output from very few laboratories around the globe.

In addition, most estimations of diffusive air–water fluxes are performed from the dissolved and gas phase concentrations, in effect, without measuring fluxes, but by estimation of the air–water mass transfer coefficient, a procedure that has important uncertainties associated to physical chemical properties (i.e., Henry's Law constant) and lack of enough knowledge on parameterization under high wind speeds and the role that the surface microlayer plays in air–water exchange under low wind speeds.

Generally, in the open ocean, the atmosphere is a net source of organic pollutants to water bodies. For example, Gioia et al. (2008a) observed air/water fugacity ratios higher than unity in some regions of the Atlantic Ocean. For the less hydrophobic POPs such as HCHs, Lakaschus et al. (2002) has suggested conditions close to equilibrium between the atmosphere and ocean. So far, the only clear example of net volatilization fluxes of organic pollutants is that described for lighter PAHs, such as phenanthrene, but it is presumably due to in-situ biogenic production of this hydrocarbon. For legacy POPs such as PCBs, Zhang and Lohmann (2010) have recently described a volatilization flux of PCBs from the south Pacific open Ocean.

At the coastal regions, volatilization of POPs is a generalized observation. For example, strong volatilization trends have been observed for the NE Atlantic Ocean (Yan et al. 2008) and the NE Mediterranean Sea (Garcia-Flor et al. 2009). Similar volatilisation fluxes have been observed for polar POPs such as nonylphenols in the NE Atlantic and North Sea (Van Ry et al. 2000; Xie et al. 2006). Volatilization fluxes of POPs from coastal waters may be the result of the important riverine and run-off fluxes into the marine environment. Coastal waters can also act as sources of POPs to open sea regions.

An issue that has received little attention so far is the relevant routes for the transport of pollutants from coastal ocean to open sea waters, and how important is this. For legacy POPs that can undergo transport through grasshopping (successive volatilization and deposition) these transfers of pollutants have been assessed implicitly when studying the air–water exchange. However, for chemicals with higher solubility and limited volatility, there is little work done on how ocean currents and mixing processes in the water column transport these chemicals in the marine environment. In the case of PFOS (Perfluorooctanesulfonic acid) and PFA (perfluoroalkoxy), it has been suggested that they could behave as passive tracers (Yamashita et al. 2008), even though this needs further research, because some of these chemicals can also undergo degradation in the environment (Yamamoto et al. 2007).

8.4 Cycle of Organic Pollutants in the Water Column

Once POPs enter in the water column through atmospheric transport or from riverine inputs, they undergo a series of environmental processes which are to a great extent related to the marine carbon cycle. POPs are hydrophobic compounds.

Hydrophibicity is assessed by the octanol-water partition coefficient (Kow), which for most POPs range from 10^4 to 10^8, and therefore, the concentrations in organic matter are 4–8 orders of magnitude higher than those in seawater. In the water column, POP will be associated to different organic matter pools contributing to the marine carbon cycle.

The aquatic carbon cycle, and specifically phytoplankton biomass, is known to play an important role in influencing the net air–water exchange by controlling the dissolved water concentration and consequently the fugacity gradient with the atmospheric gas-phase. Air–water exchange and partitioning to/uptake by phytoplankton act as coupled processes in aquatic environments (Dachs et al. 2000). Once POPs are in the dissolved phase, they may sorb to particles, and organisms such as phytoplankton, and can be removed from the surface waters and delivered to the deep ocean by sinking particles and by zooplankton vertical migration. Many studies including modeling work have shown that terrestrial organic matter (soil and forested surfaces) has an important influence on the dynamic and inventory of POPs (Eisenberg et al. 1998; Scheringer et al. 2000; Wania and McLachlan 2001). Therefore, it is logical to think that high productivity regions of the ocean may exert an important influence on the global distribution of POPs. Jurado et al. (2004) assessed the spatial and seasonal variability of the maximum reservoir capacity of the ocean compartment to act as a sink of PCBs and showed that temperature, phytoplankton biomass and mixed layer depth (MLD) can influence the reservoir capacity of the ocean (i.e., air–ocean equilibrium/storage issues). However, kinetically controlled processes such as particle settling, reactions and metabolism also need to be considered.

Despite these pieces of evidence, current evaluations on the role of oceans as reservoirs or sinks for POPs are limited to model assessments and few experimental data, reporting water concentrations in lakes and river (Totten et al. 2004; Rowe et al. 2007), but few studies have reported seawater concentrations in open ocean (Iwata et al. 1993; Schreitmuller and Ballschmiter 1994; Sobek and Gustafsson 2004; Gioia et al. 2008a, b; Nizzetto et al. 2008). Research in this field is one step behind what is known about biogenic gases such as dimethyl sulphide (DMS) and the Hg cycle and their coupling to the biological pump (Andreae and Barnard 1983; Andreae and Raemdonck 1983; Ayers and Gillet 2000).

POPs present in the ocean waters are distributed between the dissolved and particulate phases depending on sorption and desorption equilibrium with the suspended particulate matter (SPM) present in the water. Although the oceanic suspended particles are formed of a heterogeneous mixture materials derived from different abiotic and biotic sources (Swackhamer and Skoglund 1991), a large fraction of particles and aggregates are formed of different types of organic matrices and even inorganic fractions could be covered by organic films (Wania 2006). Natural organic matter suspended in the oceans primarily consists of altered biomolecules such as polysaccaharides and lipids that derived from the plankton and is subsequently modified in the water column. The classification of dissolved, colloidal and particulate phases is purely operational since in oceanic conditions there is a continuous load of organic matter from purely dissolved to large particulates. In the euphotic zone of oceans most particles in the water are planktonic living organisms like bacteria (Broman et al. 1996) and phytoplankton (Swackhamer and Skoglund 1993).

The complex mixture of natural organic matter may include different range of composition with both hydrophobic and hydrophilic parts, and may present portions of different binding capabilities (Schwarzenbach et al. 2003). This heterogeneity has direct implications for the kinetic and equilibration times of the sorptive process which cannot be explained as a simple equilibrium partitioning. While POPs may bind rapidly with the condensed "glassy" surface regions (adsorption process) in a few hours to few days, it takes periods of days or weeks to diffuse slowly into (and out of) the interior of the more flexible "soft" parts of the organic matrix (absorption processes) (Pignatello and Xing 1996; Xing and Pignatello 1997; Axelman and Broman 2001). The measured concentration in the solid phase is thus expected to vary with time (Seth et al. 1999). In addition to the natural organic matter, the fraction of organic carbon may also include other organic sorbents derived from anthropogenic activities. The most important one when considering the water-particle partitioning processes is the black carbon (BC). Such particles can be quite porous with high specific surface areas and exhibit a high affinity for many organic pollutants (particularly for compounds with planar molecular structure) (Jonker and Koelmans 2002). Therefore, the high sequestration capacities of this kind of organic materials could lead to an underestimation of predicted K_{oc} (partition coefficient between the organic carbon and the chemical) values from simple partitioning models (Gustafsson et al. 1997; Accardi-Dey and Gschwend 2003).

While particulate organic carbon (POC), and lately the fractions of soot carbon in sediments have been issues of intensive research, there are a number of issues that are still major bottlenecks in understanding of the POP cycling in the marine environment, among them the role of dissolved organic carbon as a sorbing phase and the role of the surface microlayer in atmosphere-ocean exchange of POPs.

8.4.1 Dissolved Organic Carbon

The bioavailability and behavior of POPs is influenced by POC and by the dissolved organic carbon (DOC) present in the water column. DOC in seawater is composed of a diversity of compounds with a wide molecular weight spectrum and various functional groups that exhibit different adsorption characteristics (e.g., humic substances, flulvic substances, etc.). There have been several studies of the binding capacity of DOC to POPs (Boehm and Quinn 1973; Niederer et al. 2007). The general observation is that DOM increases the apparent solubility of POPs (DOC bound phase) reducing the ability to be sequestered from the water column by the partitioning process into particles (Jaffé 1991).

DOC is the largest reservoir of OC in the oceanic environment. Current sampling methods do not allow a proper characterization of its capacity in accumulating POPs. This impedes efforts to assess its role in the global mass balance of POPs. Experimental distribution coefficients have frequently been normalized to the bulk filter-passing OC (commonly called DOC), although, this fraction contains both truly dissolved organic matter and the colloidal fraction (Gustafsson et al. 2001). Measurements of the number of colloid-sized particles (between 1 nm and a few μm in diameter) in the oceans suggest that this fraction may account for 20–50% of total DOC (Wells and Goldberg 1992; Kepkay 2000). In marine areas, DOC frequently represents more than 90% of the total OC content (TOT) in sea surface waters whereas colloidal organic materials exceeds other marine sources of POC (Kepkay 1994). Thus the presence of this material, if not accounted for, can lead to erroneous interpretations of estimated partition coefficients (Totten et al. 2001).

8.4.2 The Elusive Surface Microlayer

The surface microlayer is the thin layer in the top of the water column, with a thickness from few micrometers to 1 mm. It is thought to play an important role in a number of processes such as air–water exchanges, accumulation and degradation of POPs (Liss and Duce 1997; Cincinelli et al. 2001; Garcia-Flor et al. 2005a; Del Vento and Dachs 2007a). The importance of the surface microlayer has been recognized for several decades (MacIntyre 1974; Hardy 1982) but the study of the occurrence of POPs and processes affecting their fate and transport are limited by the sampling devices available and the small volumes of water that can be obtained from them.

The work performed so far shows that there is a high variability in the concentrations of POPs in the surface microlayer, even when consecutive samples are taken, and only part of this variability is driven by differences in OC (Garcia-Flor et al. 2005b). It is possible that this variability is intrinsic to the surface microlayer, but it is also possible that the sampling methods available introduce an additional source of variability. This large range of POP concentrations in the SML is also observed when the enrichment factors are considered from different studies (Wurl and Obbard 2004). In addition, the small volumes that can be sampled with the glass plate or metal screen makes their utility for oceanic regions very limited due to the need of larger sample volumes. In the future, the use of novel analytical techniques such as the stir bar sorbtive extraction and other novel techniques may allow to analysis of some POPs such as PAHs in the oceanic surface microlayer.

The processes driving the formation of a surface microlayer are complex, but its study is important if processes such as air–water exchange of POPs are to be understood. In the future, the development of new techniques to sample the surface microlayer, and new studies of the role of the surface microlayer on POP transport and fate are needed, which may allow to improve understanding of its affect on air–water exchange and other environmental processes.

8.4.3 Interaction Between POPs and Organic Carbon Cycle

The dynamics of POPs is intimately linked to the carbon cycle. Looking at the global distribution of OC stocks (Fig. 8.2), it appears that oceanic environment can represent an important reservoir for POPs. The sum of OC present in the global ocean waters (including biota, dissolved and particulate organic matter and superficial sediments) (~1,200 Gt) is comparable to that present in terrestrial environment (including biota, litter and humus) (~2,600 Gt).

It is believed (Jurado et al. 2004) that the total burden of PCBs present in the portion of world oceans included between the surface and the mixed layer depth (MLD) (averaging 10s–100s m) is in the order of hundreds of tons, with a considerable fraction of it associated to POC and DOC.

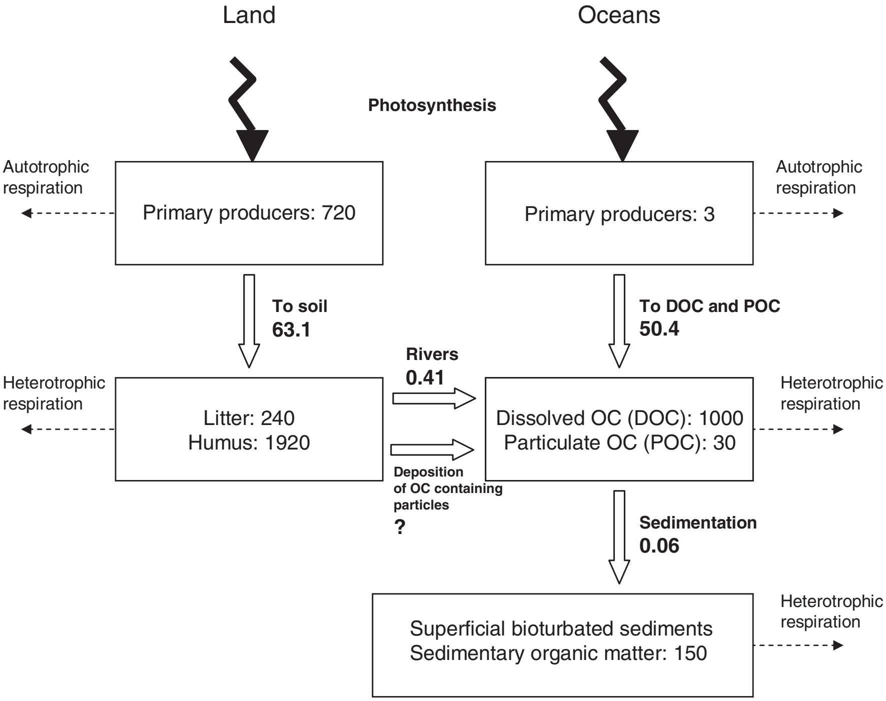

Fig. 8.2 Simplified scheme of the principal environmental stores and fluxes of OC in the biosphere. Amounts are reported in Gt (1 Gt = 10^{15} g). Fluxes are in Gt year^{-1} (Data from Ver et al. 1999; Wigely and Schimel 2000; Mackenzie and Lerman 2006)

Deeper waters are usually considered as a final sink for POPs, although an evaluation of their role in the environmental fate of POPs is not yet available. Once the POC leaves the superficial mixed waters, it sinks and supplies bounded POPs to the sediments. Sediments in coastal waters (and in particular those lying on the continental shelf) represent an important reservoir of OC and are estimated (Jönsson et al. 2003) to contain, in the superficial bioturbated layer, thousands of tons of POPs, globally.

If OC stocks control the global distribution of POPs it is reasonable to hypothesize that organic matter fluxes can serve as tracers of the potential environmental pathway of such pollutants. A key question is if it is possible to couple those two cycles in a quantitative way. Such coupling begins with the uptake on primary producers. This represents the first step for the entrance of POPs in the food webs. Autotrophic biomass is believed to be able to influence the global distribution of these pollutants, given their lipophylic characteristics and the almost ubiquitous distribution on the planet.

In the terrestrial environment this was investigated by measuring and modeling the deposition fluxes into forest ecosystems (Horstmann and McLachlan 1998; McLachlan and Horstmann 1998; Wania and McLachlan 2001). In the marine environment however, no direct observations are so far available on the potentiality of phytoplankton in influencing water column concentration. Modeling assessments (Dachs et al. 2000) suggest that phytoplankton uptake can deplete water dissolved concentration and drive significant exchange fluxes between air and water.

The OC stored in marine autotrophs, on a global scale, is much smaller than that in terrestrial phytomass (Fig. 8.2). However the net primary productivity (NPP) is comparable, because OC turnover is faster. In marine systems this can potentially make the marine primary producers a forcing parameter for the global distribution of POPs. Unfortunately, current understanding of the accumulation of POPs into phytoplankton is limited by the lack of knowledge on the actual accumulation mechanisms and the uncertainty of bioconcentration factors (Arnot and Gobas 2006). Current modeling approaches cannot adequately account for the extremely dynamic nature of the phytoplankton biomass and its interaction with the other elements of the water column. Many phytoplankton species have a life span time of 1–2 days before undergoing cellular division. The size of the phytoplankton compartment (namely: its concentration in the water) is basically the result of the balance between photosynthesis, grazing and viral lysis. Organic matter is continuously transferred to other trophic levels or to the bacterial loop and DOC is continuously generated (Handa et al. 2001). The microbial loop comprises bacteria, viruses and protozoa and controls most of the autotrophic production and grazer biomass, rather than the larger predators in the food web. The microbial loop comprises bacteria, viruses and protozoa and controls most of the autotrophic production and grazing, rather than the larger predators in the food web. However, besides the work of Wallberg and Andersson (2000) and few others, little is known about the role of the microbial loop in the fate and impact of POPs (Fig. 8.3).

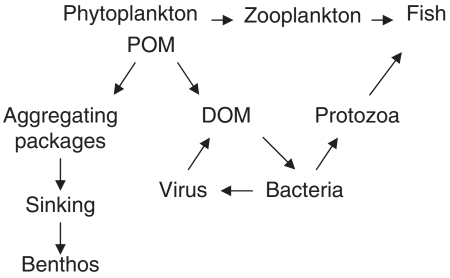

Fig. 8.3 The pelagic organic carbon pathways (Azam 1998)

During these processes, a smaller part of the POC sinks and is integrated in the superficial sediment layer, where the residual energy is basically used by the benthos. POP vertical fluxes associated to sinking particles in the water column can be directly estimated from the deposition velocity of the particles and often the fraction of OC is used as a parameter to determine the capacity in accumulating POPs. Fluxes of OC and thus of POPs associated to sinking particles are important on the continental shelves or in proximity of river estuaries, where about 97% of the total sinking organic matter deposits (Jönsson et al. 2003). In open oceanic waters most of the OC is re-mineralized within the photic zone and mesopelagic region (100–1,000 m depth).

Figure 8.3 schematizes the cycle of organic matter in the pelagic marine ecosystem. Processes occur at different spatial and temporal scales, considerably complicating the scenario. However during such processes the largest part of the organic matter (to which POP are mainly associated) entering or produced in the aquatic system is degraded and the OC is oxidized to carbon dioxide. Assuming that POPs are considerably more persistent that the organic matter, a key question concerns what happens to organic matter bound POPs during OC re-mineralization.

Recently, there has also been pointed out to the role that zooplankton has key step accumulating pollutants which are then transferred to higher trophic levels in the marine environment (Sobek et al. 2006; Berrojalbiz et al. 2009). In addition, zooplankton can accumulate organic pollutants in fecal pellets which are an important matrix for vertical transport of pollutants in the marine environment (Fowler and Knauer 1986; Dachs et al. 1996).

Current knowledge on the link between the environmental fate of POPs and OC in the biosphere is still limited. However there is evidence suggesting that autotrophic biomass accumulates a considerable fraction of the cycling POPs, and the dynamics of biomass synthesis, growth and consumption play a key role in influencing POP environmental fate. Additionally, photosynthesis, respiration and ecosystem structure are factors strictly interconnected with the climate, and therefore, sensitive to the changes occurring in it. Understanding the mechanisms linking the carbon cycle and the environmental fate of POPs is a fundamental step to assess the possible consequences which changing conditions can have on the human and ecosystem exposure to those pollutants.

8.5 Spatial Variability of Organic Pollutants in the Marine Environment

8.5.1 Geographical Variability

Data on POPs levels in the open ocean are generally scarce because sampling on research vessels requires adoption of protocols and methods to reduce contamination of the samples and the analytical challenge of measuring and detect POPs where concentrations are in the orders of pg/L in seawater and pg/m^3 in air. Generally, higher atmospheric POPs concentrations are measured in the northern hemisphere than in the southern hemisphere, which is in agreement with historical global production. For PCBs, source inventories show that the ratio of emissions between the northern and the southern hemisphere (NH:SH) is ~20:1. However, ambient levels show a smaller difference. Inaccuracies with the source inventories and/or NH “dilution” to the SH over time may explain these observations. Relatively high levels of PCBs and PAHs have been reported for the West African coast during different cruises on board two different vessels, RV Pelagia and RV Polarstern, in 2001, 2005 and 2007 respectively (Jaward et al. 2004; Del Vento and Dachs 2007b; Gioia et al. 2008a, 2010; Nizzetto et al. 2008). The sources were unknown although strong land-based emissions are suspected. Source inventories have not identified Africa as important for PCB usage raising interesting questions about unaccounted for sources/processes.

A strong latitudinal trend over the oceans is also observed within the Northern hemisphere with the highest PCB concentrations near the coasts of Europe and the lowest in the Arctic, suggests that the underlying levels in the remote Arctic atmosphere are controlled by LRAT, with deposition dominating over volatilization for PCBs in the Arctic region. Gioia et al. (2008b) raises questions about the role of ice as a compartment/buffer/source/sink for POPs in the Arctic, both in the short-term and as global climate changes occur to affect the properties and the extent of the ice sheets.

The air data show a strong decline with latitude with the highest PCB concentrations in Europe and the lowest in the Arctic. Fractionation in seawater has been observed in several studies from Europe to the Arctic Ocean (Sobek and Gustafsson 2004; Gioia et al. 2008b; Lohmann et al. 2009). In view of the different analytical procedures used by the groups, and the difficulty of comparing results from different years and somewhat different locations, the agreement between these three measurements is encouraging. However, it does restrict speculation on any trends or their absence.

8.5.2 Vertical Variability of Organic Pollutants

Unfortunately, most of the oceanic measurements of organic pollutants are made in surficial waters, usually taking advantage of the pumping systems of research ships that sample water from below the ship at 4–5 m depth. Then, the geographical variability described above is limited to samples from the upper water column, above the thermocline when the water column is stratified, and this is water influenced by atmospheric inputs as has been demonstrated by Jurado et al. (2007).

However, the oceans are notably deep, with depths of several thousands of meters in most oceanic regions. Unfortunately, there is very little information on the concentrations of POPs and the major processes affecting POPs, not only in deep waters, but also in most of the photic zone. For legacy POPs, the only vertical profiles available are those of particle phase PCBs and PAH reported for the Mediterranean and Black sea (Dachs et al. 1997a, b; Maldonado et al. 1999). These profiles show that particle phase concentrations are higher at surface and decrease with depth. Usually there is a maximum in concentrations in the photic zone that is correlated with the maximum of chlorophyll (biomass) in the water column. PCB profiles do not change through the water column, consistent with their persistence. Conversely, PAH profiles do change significantly during their transport in the water column, and while the profile of 5–6 rings PAHs is quite constant in the water column, the high predominance of 3 ring PAHs (phenanthrene, methylphenanthrenes, etc.) in the photic zone is not observed in deep waters. Low MW PAH can be degraded easily by bacteria and zooplankton (Berrojalbiz et al. 2009) and thus a major fraction of what enters the water column does not reach bottom waters.

Unfortunately, there is not a single vertical profile of dissolved phase legacy POPs available for legacy POPs. However, a few vertical profiles of emerging pollutants such as PFOS and PFOA have been recently reported (Yamashita et al. 2008). These vertical profiles show as higher concentrations at surface and an exponential decrease in concentrations with depth, the fact that these chemicals have a low affinity to sorb to particulate matter, their geographical and vertical distribution is related to marine current and the turbulent role in oceanic mixing.

8.6 Temporal Variability of Organic Pollutants in the Marine Environment

8.6.1 Long Term Trends

In general, atmospheric levels of the POPs analyzed here are declining near source regions. On the other hand, over remote areas of the open ocean it appears there is little change in air concentrations over the 15 year period (1990–2005). This points to a gradual global scale re-distribution of POPs and a shift from the dominance of primary sources to secondary sources. PCBs air concentrations over the ocean have been measured on a few different cruises in the Atlantic Ocean since 1990. Thus, a comparison of these studies may give insights into changing levels and distributions of PCBs over the Atlantic Ocean. This must be done cautiously, because they only reflect limited seasons (spring/summer in the southern hemisphere and autumn/winter in the northern hemisphere) and are subject to the uncertainties mentioned earlier (i.e., different ships, different methods and different analysts).

As mentioned earlier there are several dataset on PCBs and PAHs collected in the North and South Atlantic Ocean in the last 15 years (Schreitmuller and Ballschmiter 1994; Jaward et al. 2004; Gioia et al. 2008a, 2010). In summary, these datasets appear to have similar concentrations over the 15 year period (1990–2005), subject to the caveats made above. In contrast, several studies have shown that PCBs are declining in the atmosphere of Europe, North America and the Arctic, typically with an average half life of 4–5 years (Gioia et al. 2006). If a half life of 4–5 years is assumed to also apply to the open Atlantic Ocean, the concentration between the 1990 and 2005 should differ by about a factor of 8–10 – presumably sufficiently different to be detectable. The lack of a measured difference perhaps implies that air concentrations in these remote oceanic environments are undergoing little change, compared to the declines observed at the land-based locations close to sources. Interestingly, Panshin and Hites (1994) compared PCB in oceanic air over Bermuda in 1992/1993 with those of several studies in 1970s at the same location, and found no statistically significant difference. Hillery et al. (1997) also concluded that the atmospheric concentrations of PCBs near Lake Superior, the most remote of the Great Lakes, remained unchanged over a period of 6 years. Axelman and Broman (2001) argued that these observations indicate PCBs may be removed slowly from the environment, when viewed from a global or hemispheric perspective, with PCBs being diluted into the remote areas of the earth rather than being permanently removed from global cycling. This implies that source-region gradients would decline over time as PCBs become more uniformly distributed (Axelman et al. 2000).

8.6.2 Diel Cycling of POPs over the Ocean

Several studies on land had previously observed a strong temperature-dependent diurnal cycle for different POPs (Hornbuckle and Eisenreich 1996; Wallace and Hites 1996; Lee et al. 1998, 2000; Gouin et al. 2002; Totten et al. 2002; Lohmann et al. 2003). Jaward et al. (2004) reported for the first time a diel cycle over the open ocean for some low molecular PCBs congeners and more volatile PAHs with daytime exceeding nighttime concentrations by a factor of 1.5–2.5 in South Atlantic Ocean (Jaward et al. 2004). Such a cycle over the ocean was unrelated either to ambient or seawater temperature variations, which were insignificant between day and night. The authors suggested that the observed variability in air concentrations may be related to interactions between plankton and organic carbon concentration in the surface ocean, as a result of diel cycles in zooplankton migration, DOC cycle, and/or phytoplankton biomass turn-over, but further measurements were needed to support their hypothesis.

Since then, more data are available, confirming the presence of a diel cycle in some remote region only for more volatiles PCBs and PAHs; in contrast high molecular weight compounds did not exhibit a diurnal cycle. Ship-board atmospheric samples were collected in the North East subtropical/tropical Atlantic Ocean, at the end of spring 2003 (Del Vento and Dachs 2007b). Gas phase concentrations for some samples taken along parallel 21°N show a day/night ratios of ~1.5–2. During an Atlantic latitudinal transect in October–November 2005, air and water phases were monitoring, providing more information on the composition of the water column and its biological activity (Gioia et al. 2008a; Nizzetto et al. 2008). A diel cycle with daytime exceeding nighttime air concentrations by a factor of 1.5–3 was observed between 3°N and 27°S of the tropical South Atlantic. In this cruise dissolved phase concentrations in surface ocean also showed day/night cycled in four samples. All those observations were made on board of different ships and during different period of the year. Possible ship-borne sources were also excluded by deploy of passive samples and/or elemental and organic carbon (EC/OC) analysis. Moreover, the cycle appeared to be locally concentrated in some part of the ocean, corresponding to more oligotrophic regions, whereas ship contamination would have affected the entire datasets.

Diurnal cycling of some POPs over the ocean suggests that air concentrations, far from global source regions, are affected by some dynamic biological and/or physical processes. Water column processes affecting the carbon cycle may be drivers of air–water cycling of POPs. The influence of the “biological pump” is well documented on biogenic gases such as dimethyl sulphide (DMS) and the Hg cycle (Andreae and Barnard 1983; Andreae and Raemdonck 1983; Ayers and Gillet 2000). Phytoplankton plays an important role also on POPs, as air–water exchange and phytoplankton uptake are coupled processes (Dachs et al. 2000).

A level III/IV model, previously used to successfully interpret diel variability in PCBs air concentrations over different locations (MacLeod et al. 2007), has been used to identify possible variables that could influence the diel POPs cycle. Parameterization based on temperature, wind speed, atmospheric mixing height, and hydroxyl radical concentrations, applied to Jaward’s dataset could not explain the amplitude of diurnal POPs cycle in the atmosphere, confirming previous conclusions (Jaward et al. 2004).

Very limited information is available in the literature on other processes like zooplankton migration, microbial loop or the surface microlayer (SML) that may be involved on the diurnal cycle of POPs. The distinct chemical composition of SML promotes the accumulation of anthropogenic pollutants, such as POPs, in it and natural surfactants produced by phytoplankton can reduce air-sea gas exchange (Frew et al. 1990), but no information is available on diurnal cycles of SML properties. Existing data are therefore insufficient to explain and understand the precise mechanisms driving the diel cycle, showing that further studies are required to elucidate them.

8.7 Effects of Organic Pollutants in the Marine Environment

8.7.1 Bioconcentration, Biomagnification and Toxicological Effects

The UNEP Stockholm Convention recognizes that POPs possess toxic properties, resist degradation, bioaccumulate and are transported through air, water and migratory species, across international boundaries and deposited far from their place of release, where they accumulate in terrestrial and aquatic ecosystem (UNECE 1998). As a result, they have been found in the Arctic (Bidleman et al. 1999; Harner et al. 1998; Stern et al. 1997) and shown to bioaccumulate and biomagnify in marine mammals, polar bears and humans (Kucklick and Baker 1990; Halsall et al. 2001). There is concern for the health of indigenous Arctic people and wildlife, due to the toxicity, persistence and bioaccumulation potential of these compounds (Gilman et al. 1997). Their regulation has become an international policy issue based upon their possible effects on human health and potential environmental risks (UNECE 1998).

The concentration of a POP or metabolite increases at some of all steps in the food chain. This process is called biomagnification (Fig. 8.4), which exposes animals at high trophic levels in the food webs to doses which may causes effects such as endocrine disruption, altered neurological development, immune system modulation and cancer. Most POPs and all natural compounds which have a tendency to biomagnify in food webs are neutral organic compounds that are highly substituted (or substituted at critical positions in the molecule) with chlorine or

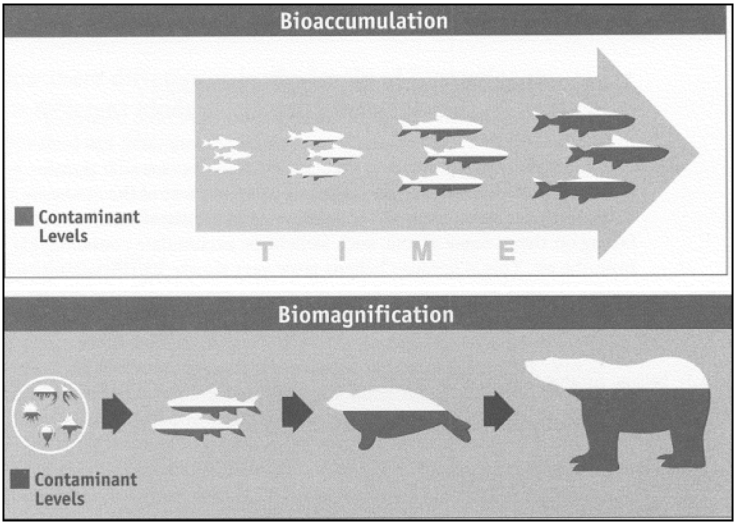

Fig. 8.4 Bioaccumulation and biomagnification

bromine. The reason for this is quite straight forward: the compounds are lipophylic and not easily metabolized. The lipophylic nature ensures efficient uptake from the diet and storage in fat depots, and the halogens block attack by enzymes. The rate of excretion of unchanged compound (usually via partitioning to feces in higher biota) is much slower than rate of uptake, so concentration in the organism becomes higher than in the diet.

It is not just the relatively non polar, lipophylic POPs and metabolites (e.g., oxychlordane and heptachlor epoxide) which bioaccumulate. Highly polar POPs (e.g., chlorophenols) are less efficiently absorbed from the gut, are relatively easily transformed into excretable metabolites, and therefore do not normally biomagnify. However, if they are formed as metabolites in the animal and protected from elimination by protein binding or some other mechanism, they may still accumulate. The first class of polar POP found to bioaccumulate was the methylsulfone metabolites of PCBs and p,p′-DDE. Methylsulfone PCBs are formed in endotherms from readily metabolized meta-/para-unsubstituted PCBs with adjacent chlorines (principally 2,5- and 2,3,6-chlorine PCBs) (Letcher et al. 1998). They are not readily further metabolized and have been shown to biomagnify in the ringed seal/polar bear food chain (Letcher et al. 1998).

Bromine is as resistant to metabolic attack as chlorine. Therefore, based on the above rules, it could have been predicted from structure alone that the brominated diphenyl ethers (BDEs) would be persistent, bioaccumulative in food webs and subject to long-range transport. However, there are several recent reports of natural organohalogen compounds which bioaccumulate in the marine environment. The most thoroughly studied has been the halogenated 1,1′-dimethyl-2,2′- bipyrroles (HDBPs), which are probably of marine bacterial origin. Four congeners are in found in marine seabirds and mammals (Tittlemier et al. 1999). All available ring carbons are substituted with halogens, ranging from Br_3Cl_3 to Br_4, and the two aromatic nitrogens are bonded to methyl groups. These compounds have been shown to biomagnify in an Arctic marine food web up to seabirds (but not seals) to nearly the same extent as persistent PCBs, and to have similar physical–chemical properties. This is the first report of a biomagnifying natural compound. The structure of these compounds fits well within the rules for biomagnification in terrestrial endotherms that were developed for anthropogenic organohalogen compounds.

An issue that has received increasing attention during the last decades is the effect of organic pollutants to the first steps of the trophic web, phytoplankton, bacteria and zooplankton. This is relevant because in terms of fluxes of carbon, these are the major vectors for carbon fluxes and cycling in the marine environment. A small effect of organic pollutants in phytoplankton or bacteria can induce a high effect in terms of perturbation of the carbon fluxes. In addition, there is modeling work that shows that indirect effects of pollutants can be found at high levels of the trophic web even though the pollutant is only toxic at lower trophic levels (Bacelar et al. 2009).

The previous work on phytoplankton sensitivity to organic pollutants has being made studying the effects of herbicides in coastal regions and the influence on PAHs on phytoplankton including the role of phototoxicity (DeLorenzo and Serrano 2003; Grote et al. 2005; Pelletier et al. 2006; Petersen and Dahllöf 2007). These studies show that indeed organic pollutants can affect the photosynthesis system and decrease the abundance of phytoplankton communities in the marine environment. The work done so far, shows that the effects are observed at concentrations higher than those measured in open ocean waters. However, these studies have been done for a single chemical or a simple mixture of chemicals, which in the marine environment there are thousands of chemicals that can have synergistic, or just additive effects (Dachs and Méjanelle 2010). In addition, the effects are not observed at the same concentrations for all phytoplankton species. Recently, Echeveste et al. have shown that the concentration at which the effect is observed depends on the cell size, being the small organisms, *Prochlorococcus* sp. and *Synechococcus* sp., mainly, the more sensible to organic pollutants such as PAHs (Echeveste et al. 2010). These pioneering studies show that there is need for a more comprehensive assessment of the effects of real mixtures of organic pollutants to phytoplankton, bacteria and zooplankton in order to determine whether there is a significant coupling between POP occurrence in the ocean and the major vectors of organic matter in oceanic waters.

8.8 Oceanic Sinks of Organic Pollutants

In addition to covering a major fraction of the earth’s surface, the oceans can be deep, with well developed vertical structures due to physical barriers of stratification, or incomplete mixing or biological activity mainly concentrated at the top 100 m. Vertical transport of pollutants in the marine environment can occur as associated to particulate matter and due to physical mixing. For hydrophobic POPs, the biological pump mediates the oceanic sink of POPs. Indeed, pollutants sorb to phytoplankton and other organic matter pools, a fraction of this organic matter settles to the deep ocean and carries the organic matter-bound POPs (Dachs et al. 1996, 2002; Fowler and Knauer 1986). In addition, the biological pump plays also an important role be decreasing the dissolved concentrations, thus modifying the air–water gradient in concentrations which leads to enhanced air–water fluxes of POPs. Dachs et al. assessed the role of the biological pump at the global scale. They reached the conclusion that increased fluxes were found at high latitudes and in other regions with high primary productivity such as upwelling regions. The role of the biological pump is more important for the more hydrophobic compounds. Jurado and Dachs (2008) have also shown that the biological pump can considerably reduce the atmospheric residence times of hydrophobic POPs. The mechanisms currently taken into account when estimating the role of the biological pump are in fact a simplification of the complex nature of the processes driving the vertical fluxes of POPs, but it provides a reasonable estimation of the magnitude of the biological pump. Figure 8.5 shows the comparison of the measured fluxes measured in the north Atlantic (Gustafsson et al. 1997), the Mediterranean sea

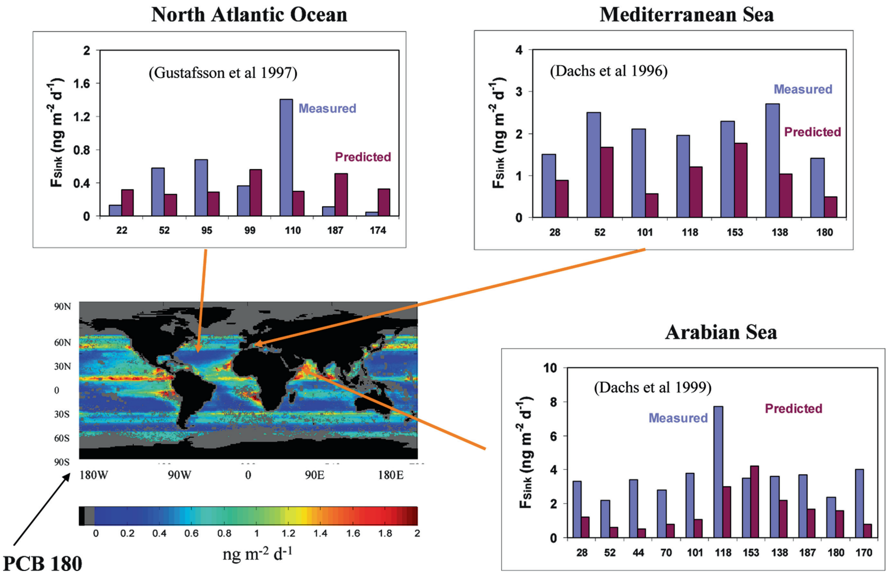

Fig. 8.5 Comparison of measured settling fluxes of PCBs and predicted fluxes (From Dachs et al. 2002) for the Mediterranean Sea, the Arabian Sea and the north Atlantic Ocean

(Dachs et al. 1996), and the Arabian sea (Dachs et al. 1999) with the predictions from current models of the role of the biological pump. It shows that predictions of settling fluxes are usually within a factor of three of predictions, and this gives an idea of the uncertainty associated with current models of the marine POPs. In order to improve these predictions, a better knowledge of processes driving the fluxes of organic matter and associated pollutants should be obtained. Jurado et al. (2004 and 2005) have provided for example the overall magnitude of the Atlantic ocean sink of PCBs and PCDDFs, and Lohmann et al. (2006) have shown that this is the main global sink for the more hydrophobic chemicals, while the atmosphere (due to reaction with OH radicals) may be the dominating sink for the less hydrophobic POPs.

Recently, Lohmann et al. (2006) estimated the magnitude of the physical pump for PCBs. The physical pump is due to the subduction of large masses of water in the Ross Sea, the Weddell Sea, the Greenland current and Labrador Sea. They showed that the physical pump is more important in magnitude regionally than the biological pump, but when integrated at the global scale, the biological pump is still the main oceanic sink of hydrophobic POPs.

The biological pump will also be the major sink for other hydrophobic POPs such as polybrominated biphenyl ethers, even though this has not been quantified so far. However, some emerging POPs such as perfluorinated compounds have different physical–chemical properties and can be considered as "swimmers" because they do not adsorb much to organic matter and are found mainly in the dissolved phase. Yamashita et al. (2008) has suggested that they behave as passive tracers, thus following marine currents and turbulent mixing. However, the magnitude of the oceanic sink for these chemicals has not yet being estimated.

8.9 Major Unknowns, Conclusions, and the Challenges for Future Research

Even though the study of the oceanic POPs has been active since the early days of the research on the environmental chemistry of POPs (Bidleman and Olney 1974), the field has been limited by the methods available for the measurement of oceanic POPs. However, during the last decade, the amount of research on oceanic POPs has increased considerably and the role of oceanic sinks and cycling has been recognized as key for understanding the global dynamics of POPs. However, the field still needs of the development of new techniques to better estimate the different pools of POPs in oceanic waters, to estimate the coupling of the cycle of POPs with the cycle of organic matter, and the oceanic sinks. In addition, the field would benefit from techniques that could allow increases in the number and frequency of samples analyzed, if not of continuous measurements, so that processes can be better understood.

One of the major unknowns is the vertical distribution of POPs in the ocean. There is not a single vertical profile of POPs in the dissolved phase, and this lack of knowledge introduces a huge uncertainty in current global mass balances and assessment of global sinks of POPs. Other issues that will receive much attention during the coming years are the effects that complex mixtures of POPs and other compounds play as environmental stressors of phytoplankton, zooplankton, the microbial loop and rest of oceanic biota.

Because of the fast development during the last decades of the global economy, the use of resources has increased exponentially, and presumably the number of organic chemicals that have entered the environment has also being increasing. Even though not all these chemicals will be persistent, a fraction of them may persist in the environment for decades, in fact, every year there are new pollutants that are “discovered” in the environment. Their introduction should be viewed as another vector of current global change which represents an additional stressor for organisms, communities and ecosystems that is largely not understood.

References

Accardi-Dey, A. and P.M. Gschwend, 2003: Reinterpreting literature sorption data considering both absorption into organic carbon and adsorption onto black carbon. Environ. Sci. Technol. 37, 99–106.

Andreae, M.O. and H. Raemdonck, 1983a: Dimethyl sulfide in the surface ocean and the marine atmosphere: A global view. Science 221, 744–747.

Andreae, M.O. and W.R. Barnard, 1983b: Determinations of trace quantities of dimethyl sulfide in aqueous solutions. Anal Chem. 55, 608–612.

Arnot, J.A. and F.A.P.C. Gobas, 2006: A review of bioconcentration factor (BCF) and bioaccumulation factor (BAF) assessments for organic chemicals in aquatic organisms. Environ. Rev. 14, 257–297.

Axelman, J., D. Broman, and C. Näf, 2000: Vertical flux and particulate/water dynamics of Polychlorinated Biphenyls (PCBs) in the open Baltic sea. Ambio 29, 210–216.

Axelman, J. and D. Broman, 2001: Budget calculations for polychlorinated biphenyls (PCBs) in the Northern Hemisphere – a single-box approach. Tellus 53B, 235–259.

Ayers, G.P. and R.W. Gillet, 2000: DMS and its oxidation products in the remote marine atmosphere: Implications for climate and atmospheric chemistry. J. Sea Res. 43, 275–286.

Azam, F., 1998: Microbial control of oceanic carbon loop: The plot thickens. Science 280, 694–696.

Bacelar, F.S., S. Dueri, E. Hernández-García, and J.M. Zaldivár, 2009: Joint effects of nutrients and contaminants on the dynamics of a food chain in marine ecosystems. Math. Biosci. 218, 24–32.

Berrojalbiz, N., S. Lacorte, A. Calbet, E. Saiz, C. Barata, and J. Dachs, 2009: Accumulation and cycling of polycyclic aromatic hydrocarbons in zooplankton. Environ. Sci. Technol. 43, 2295–2301.

Bidleman, T.F. and C.E. Olney, 1974: Chlorinated hydrocarbons in the Sargasso Sea atmosphere and surface water. Science 183, 516–518.

Bidleman T.F., G.W. Patton, D.A. Hinckley, M.D. Walla, W.E. Cotham, and B.T. Hargrave, 1999: Chlorinated pesticides and polychlorinated biphenyls in the atmosphere of the Canadian Arctic. In: Kurtz, D. (Ed.), Long-Range Transport of Pesticides, Lewis Publisher, Chelsea, MI.

Boehm, P.D. and J.G. Quinn, 1973: Solubilization of hydrocarbons by the dissolved organic matter in sea water. Geochim. Cosmochim. Acta 37, 2459–2477.

Broman D., C. Näf, J. Axelman, C. Bandh, H. Pettersen, R. Johnstone, and P. Wallberg, 1996: Significance of bacteria in marine waters for the distribution of hydrophobic organic contaminants. Environ. Sci. Technol. 30, 1238.

Cincinelli, A., A.M. Stortini, M. Perugini, L. Checchini, and L. Lepri, 2001: Organic pollutants in sea surface microlayer and aerosol in the coastal environment of Leghorn (Tyrrhenian Sea). Mar. Chem. 76, 77–98.

Crutzen, P.J. and E.F. Stoermer, 2000: The "Anthropocene". Global Change Newsl. 41, 17–18.

Dachs, J., J.M. Bayona, S.W. Fowler, J.C. Miquel, and J. Albaigés, 1996: Vertical fluxes of polycyclic aromatic hydrocarbons and organochlorine compounds in the western Alboran Sea (southwestern Mediterranean). Mar. Chem. 52, 75–86.

Dachs, J., J.M. Bayona, C. Raoux, and J. Albaigés, 1997a: Spatial, vertical distribution and budget of polycyclic aromatic hydrocarbons in the western Mediterranean seawater. Environ. Sci. Technol. 31, 682–688.

Dachs, J., J.M. Bayona, and J. Albaigés, 1997b: Spatial distribution, vertical profiles and budget of organochlorine compounds in Western Mediterranean seawater. Mar. Chem. 57, 313–324.

Dachs, J., J.M. Bayona, J. Fillaux, A. Saliot, and J. Albaigés, 1999: Evaluation of anthropogenic and biogenic inputs into the western Mediterranean using molecular markers. Mar. Chem. 65, 195–210.

Dachs, J., S.J. Eisenreich, and R.M. Hoff, 2000: Influence of eutrophication on air–water exchange, vertical fluxes and phytoplankton concentrations of persistent organic pollutants. Environ. Sci. Technol. 34, 1095–1102.

Dachs, J., R. Lohmann, W.A. Ockenden, L. Mejanelle, S.J. Eisenreich, and K.C. Jones, 2002: Oceanic biogeochemical controls on global dynamics of persistent organic pollutants. Environ. Sci. Technol. 36, 4229–4237.

Dachs, J. and L. Méjanelle, 2010: Organic pollutants in coastal waters, sediments and biota: A relevant driver for ecosystems during the anthropocene? Estuar. Coast. 33, 1–14.

DeLorenzo, M.E and L. Serrano, 2003: Individual and mixture toxicity of three pesticides; atrazine, chlorpyrifos, and chlorothalonil to the marine phytoplankton species *Dunaliella tertiolecta*. J. Environ. Sci. Health Part B, B38 (5), 529–538.

Del Vento, S. and J. Dachs, 2007a: Influence of the surface microlayer on atmospheric deposition of aerosols and polycyclic aromatic hydrocarbons. Atmos. Environ. 41, 4920–4930.

Del Vento, S. and J. Dachs, 2007b: Atmospheric occurrence and deposition of polycyclic aromatic hydrocarbons in the northeast tropical and subtropical Atlantic Ocean. Environ. Sci. Technol. 41, 5608–5613.

Donkin, P., E.L. Smith, and S.J. Rowland, 2003: Toxic effects of unresolved complex mixtures of aromatic hydrocarbons accumulated by mussels, *Mytilus Edulis*, from contaminated field sites. Environ. Sci. Technol. 37, 4825–4831.

Echeveste, P., S. Agustí, and J. Dachs, 2010: Cell size dependent toxicity thresholds of polycyclic aromatic hydrocabons to cultured and natural phytoplankton populations. Environ. Pollut. 158, 299–307.

Eisenberg, J.N.S., D.H. Bennett, and T.E. Mckone, 1998: Chemical dynamics of persistent organic pollutants: A sensitivity analysis relating soil concentration levels to atmospheric emissions. Environ. Sci. Technol. 32, 115–123.

Farré, M., S. Pérez, L. Kantiani, and D. Barceló, 2008: Fate and toxicity of emerging pollutants, their metabolites and transformation products in the aquatic environment. Trends. Anal. Chem. 27, 991–1007.

Fowler, S.W. and G.A. Knauer, 1986: Role of large particles in the transport of elements and organic compounds through the oceanic water column. Progr. Oceanogr. 16, 147–194.

Frew, N.M., J.C. Goldman, M.R. Dennett, and A.S. Johnson, 1990: Impact of phytoplankton-generated surfactants on air–sea gas exchange. J. Geophys. Res. Ocean 95, 3337–3352.

Garcia-Flor, N., C. Guitart, M. Ábalos, J. Dachs, J.M. Bayona, and J. Albaigés, 2005a: Enrichment of organochlorine compounds in the sea surface microlayer: An organic carbon driven process. Mar. Chem. 96, 331–345.

Garcia-Flor, N., C. Guitart, L. Bodineau, J. Dachs, J.M. Bayona, and J. Albaigés, 2005b: Comparison of sampling devices for the determination of polychlorinated biphenyls in the sea surface microlayer. Mar. Environ. Res. 59, 255–275.

Garcia-Flor, N., J. Dachs, J.M. Bayona, and J. Albaigés, 2009: Surface waters are a source of polychlorinated biphenyls to the coastal atmosphere of the north-western Mediterranean Sea. Chemosphere 75, 1144–1152.

Gilman, A., E. Dewailly, M. Feeley, V. Jerome, H. Kuhnlein, B. Kwavnick, S. Neve, B. Tracy, P. Usher, J. Van Oostdam, J. Walker, and B. Wheatley, 1997: Chapter 4: Human health. In: Jensen, J., K. Adhare, R. Shearer (Eds.), Canadian Arctic Contaminants Assessment Report, Department of Indian and Northern Affairs, Ottawa, pp. 295–377.

Gioia, R., E. Steinnes, G.O. Thomas, .S.N. Meijer, and K.C. Jones, 2006: Persistent organic pollutants in European background air: Derivation of spatial and temporal trends. J. Environ. Monitor. 8, 700–710.

Gioia, R, L. Nizzetto, R. Lohmann, J. Dachs, and K.C. Jones: 2008a: Polychlorinated biphenyls (PCBs) in air and seawater of the Atlantic Ocean: Sources, trends and processes. Environ. Sci. Technol. 42, 1416–1422.

Gioia, R., R. Lohmann, J. Dachs, C. Temme, S. Lakaschus, D. Schulz-Bull, I. Hand, and K.C. Jones, 2008b: Polychlorinated biphenyls in air and seawater of the North Atlantic and the Arctic Ocean, J. Geophys. Res. 113, D19302, doi: 10.1029/2007JD009750.

Gioia, R., S. Eckhardt, K. Breivik, F.M. Jaward, A. Prieto, L. Nizzetto, and K.C. Jones, 2011: Evidence for Major Emissions of PCBs in the West African Region. Environ. Sci. Technol. 45(4), 1349–1355.

Gomez-Gutierrez, A.I., E. Jover, L. Bodineau, J. Albaigés, and J.M. Bayona, 2006: Organic contaminant loads into the Western Mediterranean Sea: Estimate of Ebro River inputs. Chemosphere 65, 224–236.

Gouin, T., G.O. Thomas, I. Cousins, J. Barber, D. Mackay, and K.C. Jones, 2002: Air-surface exchange of polybrominated diphenyl ethers and polychlorinated biphenyls. Environ. Sci. Technol. 38, 1426–1434.

Grote, M., G. Schüürmann, and R. Altenburger, 2005: Modelling photoinduced algal toxicity of polycyclic aromatic hydrocarbons. Environ. Sci. Technol. 39, 4141–4149.

Gustafsson, Ö., F. Haghseta, C. Chan, J. Macfarlane, and P.M. Gschwend, 1997: Quantification of the dilute sedimentary soot phase: Implications for PAH speciation and bioavailability. Environ. Sci. Technol. 31, 203–209.

Gustafsson, Ö. and P.M. Gschwend, 1997: Aquatic colloids: Concepts, definitions, and current challenges. Limnol. Oceanogr. 42, 519–528.

Gustafsson, Ö., N. Nilsson, and T.D. Bucheli, 2001: Dynamic colloid-water partitioning of pyrene through a coastal baltic spring bloom. Environ. Sci. Technol. 35, 4001–4006.

Halsall, C.J., A.J. Sweetman, L.A. Barrie, and K.C. Jones, 2001: Modelling the behaviour of PAHs during atmospheric transport from the UK to the Arctic. Atmos. Environ. 35, 255–267.

Handa, N., E. Tanoue, and T. Hama, 2001: Dynamics and Characterization of Marine Organic Matter, Kluwer Academic Publisher, London, 560pp.

Hardy, J.T., 1982: The sea surface microlayer: Biology, chemistry and anthropogenic enrichment. Progr. Oceanogr. 11, 307–328.

Harner, T., H. Kylin, T.F. Bidleman, C. Halsall, W.J. Strachan, L. Barrie, and P. Fellin, 1998: Polychlorinated naphtalenes and coplanar polychlorinated byphenyls in Arctic air. Environ. Sci. Technol. 32, 3257–3265.

Hillery, B.R., I. Basu, C.W. Sweet, and R.A. Hites, 1997: Temporal and spatial trends in a long-term study of gas-phase PCB concentrations near the Great Lakes. Environ. Sci. Technol. 31, 1811–1816.

Hornbuckle, K.C., C.W. Sweet, R.F. Pearson, and D.L. Swackhamer, 1995: Assessing annual water–air fluxes of polychlorinated biphenyls in Lake Michigan. Environ. Sci. Technol. 29, 869–877.

Hornbuckle, K.C. and S.J. Eisenreich, 1996: Dynamics of gaseous semivolatile organic compounds in a terrestrial ecosystem-effects of diurnal and seasonal climate variations. Atmos. Environ. 30, 3935–3945.

Horstmann, M. and M.S. McLachlan, 1998: Atmospheric deposition of semivolatile organic compounds to two forest canopies. Atmos. Environ. 32, 1799–1809.

Iwata, I., S. Tanabe, N. Sakai, and R. Tatsukawa, 1993: Distribution of persistent organochlorines in the oceanic air and surface seawater and the role of ocean on their global transport and fate. Environ. Sci. Technol. 27, 1080–1098.

Jaffé, R., 1991: Fate of hydrophobic organic pollutants in the aquatic environment: A review. Environ. Pollut. 69, 237–257.

Jahnke, A., U. Berger, R. Ebinghaus, and C. Temme, 2007: Latitudinal gradient of airborne polyfluorinated alkyl substances in the marine atmosphere between Germany and South Africa (53 degrees N-33 degrees S). Environ. Sci. Technol. 41, 3055–3061.

Jaward, F.M., S.N. Meijer, E. Steinnes, G.O. Thomas, and K.C. Jones, 2004: Further studies on the latitudinal and temporal trends of persistent organic pollutants in Norwegian and U.K. background air. Environ. Sci. Technol. 38, 2523–2530.

Jonker, M.T. and A.A. Koelmans, 2002: Sorption of polycylic aromatic hydrocarbons and polychlorinated biphenyls in soot and soot-like materials in the aqueous environment: mechanistic considerations. Environ. Sci. Technol. 36, 3725–3734.

Jönsson, A., Ö. Gustafsson, J. Axelman, and H. Sundberg, 2003: Global accounting of PCBs in the continental shelf sediments. Environ. Sci. Technol. 37, 245–255.

Jurado, E., R. Lohmann, S. Meijer, K.C. Jones, and J. Dachs, 2004: Latitudinal and seasonal capacity of the surface ocean as a reservoir of polychlorinated biphenyls. Environ. Pollut. 128, 149–162.

Jurado, E., F. Jaward, R. Lohmann, K.C. Jones, R. Simó, and J. Dachs, 2005: Wet deposition of persistent organic pollutants to the global oceans. Environ. Sci. Technol. 39, 2426–2435.

Jurado, E., J. Dachs, D. Marinov, and J.M. Zaldivar, 2007: Fate of persistent organic pollutants in the water column: Does turbulent mixing matter? Mar. Pollut. Bull. 54, 441–451.

Jurado, E. and J. Dachs, 2008: Seasonality in the "grasshopping" and atmospheric residence times of persistent organic pollutants over the oceans. Geophys. Res. Lett. 35, L17805, doi: 10.1029/2008GL034698.

Kasprzyk-Hordern, B., R.M. Dinsdale, and A.J. Guwy, 2008: The occurrence of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs in surface water in South Wales. UK Water Res. 42, 3498–3518.

Kepkay, P.E., 1994: Particle aggregation and the biological reactivity of colloids. Mar. Ecol. Prog. Ser. 109, 293–304.

Kepkay, P.E., 2000: Colloids and the ocean carbon cycle. In: Wangersky, PJ (Ed.), The Handbook of Environmental Chemistry, Part D: Marine Chemistry, Springer-Verlag, New York, pp. 35–56.

Kucklick, J.R. and J.E. Baker, 1990: Organochlorines in Lake Superior's food web. Environ. Sci. Technol. 32, 1192–1198.

Lakaschus, S., K. Weber, F. Wania, R. Bruhn, and O. Schrems, 2002: The air−sea equilibrium and time trend of hexachlorocyclohexanes in the Atlantic Ocean between the Arctic and Antarctica. Environ. Sci. Technol. 36,138–145.

Lee, R.G.M., V. Burnett, T. Harner, and K.C. Jones, 2000: Gas-particle partition measurements of PAHs at Hazelrigg, UK. Environmental Science and Technology, 34(3). pp. 393–398. ISSN 0013-936X.

Lee, R.G.M., H. Hung, D. Mackay, and K.C. Jones, 1998: Measurement and modelling of the diurnal cycling of atmospheric PCBs and PAHs. Environ. Sci. Technol. 32, 2172–2179.

Letcher, R.J., R.J. Norstrom, and D.C.G. Muir, 1998: Biotransformation versus bioaccumulation: Sources of methyl sulfone PCB and 4,4′-DDE metabolites in the polar bear food chain, Environ. Sci. Technol. 32, pp. 1656–1661.

Li, Y.H., 2000: A Compendium of Geochemistry, Princeton University Press, Princeton, NJ, 475 pp.

Liss, R.S. and R.A. Duce, 1997: The Sea Surface and Global Change, Cambridge University Press, Cambridge, UK.

Lohmann, R., P.A. Brunciak, J. Dachs, C.L. Gigliotti, E. Nelson, D. Van Ry, T. Glenn, S.J. Eisenreich, J.L. Jones, and K.C. Jones, 2003: Processes controlling diurnal variations of PCDD/Fs in the New Jersey coastal atmosphere. Atmos. Environ. 37, 959–969.

Lohmann, R., E. Jurado, J. Dachs, and K.C. Jones, 2006: Quantifying the importance of the atmospheric sink of polychlorinated dibenzo dioxins and furans relative to other global loss processes. J. Geophys. Res. 111, D21303, doi: 10. 1029/2005JD006983.

Lohmann, R., K. Breivik, J. Dachs, and D. Muir, 2007: Global fate of POPs: Current and future research trends. Environ. Pollut. 150, 150–186.

Lohmann, R., R. Gioia, K.C. Jones, L. Nizzetto, C. Temme, Z. Xie, D. Schulz-Bull, E. Morgan, and L. Jantunen, 2009: Organochlorine pesticides and PAHs in the surface water and atmosphere of the North Atlantic and Arctic Ocean. Environ. Sci. Technol. 43, 5633–5639.

Mackenzie, F.T. and A. Lerman, 2006: Carbon in the Geosphere – Earth's Outer Shell, Springer, Dordrecht, The Netherlands, 402pp.

Maldonado, C., J. Dachs, and J.M. Bayona, 1999: Trialkylamines and coprostanol as tracers of urban pollution in waters from enclosed seas: The Mediterranean and Black Sea. Environ. Sci. Technol. 33, 3290–3296.

MacIntyre, F., 1974: The top millimeter of the ocean. Sci. Am. 230, 62–69.

MacLeod, M., M. Scheringer, H. Podey, K.C. Jones, and K. Hungerbühler, 2007: The origin and significance of short-term variability of semi-volatile contaminants in air. Environ. Sci. Technol. 41, 3249–3253.

McLachlan, M.S. and M. Horstmann, 1998: Forests as filters of airborne organic pollutants: A model. Environ. Sci. Technol. 32, 413–420.

Melbye, A.G., O.G. Brakstad, J.N. Hokstad, I.K. Gregersen, B.H. Hansen, A.M. Booth, S.J. Rowland, and K.E. Tollefsen, 2009: Chemical and toxicological characterization of an unresolved complex mixture-rich biodegraded crude oil. Environ. Toxicol. Chem. 28, 1815–1824.

Muir, D.C.G. and P.H. Howard, 2006: Are there new persistent organic pollutants? A challenge for environmental chemists. Environ. Sci. Technol. 40, 7157–7166.

Nelson, E.D., L.L. McConnell, and J.E. Baker, 1998: Diffusive exchange of gaseous polycyclic aromatic hydrocarbons and polychlorinated biphenyls across the air–water interface of the Chesapeake Bay. Environ. Sci. Technol. 32, 912–919.

Niederer, C., R.P. Schwarzenbach, and K.-U. Goss, 2007: Elucidating differences in the sorption properties of 10 humic and fulvic acids for polar and nonpolar organic chemicals. Environ. Sci. Technol. 41, 6711–6717.

Nizzetto, L., R. Lohmann, R. Gioia, A. Jahnke, C. Temme, A. Di Guardo, and K.C. Jones, 2008: PAHs in air and seawater along a North-South Atlantic transect: Trends and controlling processes. Environ. Sci. Technol. 42, 1580–1585.

Panshin, S.Y. and R.A. Hites, 1994: Polychlorinated concentrations of polychlorinated biphenyls at Bermuda. Environ. Sci. Technol. 28, 2001–2007.

Pelletier, E., P. Sargian, J. Payet, and S. Demers, 2006: UV effects on aquatic and coastal ecosystems ecotoxicological effects of combined UVB and organic contaminants in coastal waters: A review. Photochem. Photobiol. 82, 981–993, doi: 2005-09-18-RA-688.

Petersen, D.G. and I. Dahllöf, 2007: Combined effects of Pyrene and UV-light on algae and bacteria in an Arctic sediment. Ecotoxicology 16, 371–377.

Pignatello, J.J. and B. Xing, 1996: Mechanisms of slow sorption of organic chemicals to natural particles. Environ. Sci. Technol. 30, 1–11.

Pistochi, A. and R. Loos, 2009: A map of European emissions and concentrations of PFOS and PFOA. Environ. Sci. Technol. 43, 9237–9244.

Postigo, C., M.J. López de Alda, and D. Barceló, 2009: Drugs of abuse and their metabolites in the Ebro River basin: Occurrence in sewage and surface water, sewage treatment plants removal efficiency, and collective drug usage estimation. Environ. Int. doi: 10.1016/j.envint.2009,10.004.

Rowe, A., L.A. Totten, M. Xie, T.J. Fikslin, and S.J. Eisenreich, 2007: Air–water exchange of polychlorinated biphenyls in the Delware River. Environ. Sci. Technol. 41, 1152–1158

Rowland, S., P. Donkin, E. Smith, and E. Wraige, 2001: Aromatic hydrocarbon "humps" in the marine environment: unrecognized toxins? Environ. Sci. Technol. 35, 2640–2644.

Scheringer, M., F. Wegmann, K. Fenner, and K. Hungerbühler, 2000: Investigation of the cold condensation of persistent organic pollutants with a global multimedia fate model. Environ. Sci. Technol. 34, 1842–1850.

Schreitmuller, J. and K. Ballschmiter, 1994: Fresenius. J. Anal. Chem. 348, 226–239.

Schwarzenbach, R.P., P.M. Gschwend, and D.M. Imboden, 2003: Environmental Organic Chemistry, Willey, NJ.

Seth, R., D. Mackay, and J. Muncke, 1999: Estimating the organic carbon partition coefficient and its variability for hydrophobic chemicals. Environ. Sci. Technol. 33, 2390–2394.

Sobek, A. and Ö. Gustafsson, 2004: Latitudinal fractionation of poly-chlorinated biphenyls in surface seawater along a 62° N–89° N transect from the Southern Norwegian Sea to the North Pole area, Environ. Sci. Technol. 38, 2746–2751.

Sobek, A., K. Olli, and Ö. Gustafsson, 2006: On the relative significance of bacteria for the distribution of polychlorinated biphenyls in Arctic Ocean surface waters. Environ. Sci. Technol. 40, 2586–2593.

Steffen, W., P.J. Crutzen, and J.R. McNeill, 2007: The anthropocene: Are humans now overwhelming the great forces of nature? Ambio 36, 614–621.

Stern, G.A., C.A. Halsall, L.A. Barrie, D.C.G. Muir, P. Fellin, B. Rosenberg, F. Ya. Rovinsky, E. Ya. Kononov, and B. Pastuhov, 1997: Polychlorinated biphenyls in Arctic air. 1. Temporal and spatial trends. 1992–1994. Environ. Sci. Technol. 31, 3619–3628.

Swackhamer, D.L. and R.S. Skoglund, 1991: The role of phytoplankton in the partitioning of hydrophobic organic contaminants in water. In: Baker, R. (Ed.), Organic Substances and Sediments in Water, Lewis publishers, Chelsea, MI, II: pp. 91–105.

Swackhamer, D.L. and R.S. Skoglund, 1993: Bioaccumulation of PCBs by algae: Kinetics versus equilibrium. Environ. Toxicol. Chem. 12, 831.

Tittlemier, S.A., M. Simon, W.M. Jarman, J.E. Elliott, and R.J. Norstrom, 1999: Identification of a novel $C_{10}H_6N_2Br_4Cl_2$ heterocyclic compound in seabird eggs. A bioaccumulating marine natural product? Environ. Sci. Technol. 33, 26–33.

Totten, L.A., P.A. Brunciak, C.L. Gigliotti, J. Dachs, T.R. Glenn, E.D. Nelson, and S.J. Eisenreich, 2001: Dynamic air–water exchange of polychlorinated biphenyls in the New York–New Jersey Harbor estuary. Environ. Sci. Technol. 35, 3834–3840.

Totten, L.A., S.J. Eisenreich, and P.A. Brunciak, 2002: Evidence for destruction of PCBs by the OH radical in urban atmospheres. Chemosphere 47, 735–746.

Totten, L.A., C.L. Gigliotti, D.A. Van Ry, J.H. Offenberg, E.D. Nelson, J. Dachs, J.R. Reinfelder, and S.J. Eisenreich, 2004: Atmospheric concentrations and deposition of polychlorinated biphenyls to the Hudson River Estuary. Environ. Sci. Technol. 38, 2568–2573.

UNECE, 1998: Protocol to the 1979 Convention on Long-Range Transboundary Air Pollution on Persistent Organic Pollutants, United Nations Economic Commission for Europe, Aarhus, Denmark.

UNEP, 2001: Final Act of the Plenipotentiaries on the Stockholm Convention on Persistent organic Pollutants, United Nations environment program chemicals, Geneva, Switzerland, 445pp.

Van Ry, D.A., J. Dachs, C.L. Gigliotti, P. Brunciak, E.D. Nelson, and S.J. Eisenreich, 2000: Atmospheric seasonal trends and environmental fate of alkylphenols in the Lower Hudson River estuary. Environ. Sci. Technol. 34, 2410–2417.

Ver, L.M.B., F.T. Mackenzie, and A. Lerman, 1999: Biogeochemical responses of the carbon cycle to natural and human perturbation: Past, present and future. Am. J. Sci. 299, 762–801.

Wallace, J.C. and R.A. Hites, 1996: Diurnal variations in atmospheric concentrations of polychlorinated biphenyls and endosulfan: Implications for sampling protocols. Environ. Sci. Technol. 30, 444–446.

Wallberg, P. and A. Andersson, 2000: Transfer of carbon and polychlorinated biphenyl through the pelagic microbial food web in a coastal ecosystem. Environ. Toxicol. Chem. 18, 1250–1257.

Wania, F. and D. Mackay, 1996: Tracking the distribution of persistent organic pollutants. Environ. Sci. Technol. 30, 390A–396A.

Wania, F. and M.S. McLachlan, 2001: Estimating the influence of forests on the overall fate of semivolatile organic compounds using a multimedia fate model. Environ. Sci. Technol. 35, 582–590.

Wania, F., 2006: Potential of degradable organic chemicals for absolute and relative enrichment in the Arctic. Environ. Sci. Technol. 40, 569–577.

Wells, M.L. and E.D. Goldberg, 1992: Marine submicron particles. Mar. Chem. 40, 5–18.

Wigely, T.M.L. and D.S. Schimel, 2000: The Carbon Cycle, Cambridge University Press, Cambridge, UK, 292pp.

Wurl, O. and J.P. Obbard, 2004: A review of pollutants in the sea-surface microlayer (SML): A unique habitat for marine organisms. Mar. Pollut. Bull. 48, 1016–1030.

Xie, Z., S. Lakaschus, R. Ebinghaus, A. Caba, and W. Ruck, 2006: Atmospheric concentrations and air-sea exchanges of nonylphenol, tertiary octylphenol and nonylphenol monoethoxylate in the North Sea. Environ. Pollut. 142, 170–180.

Xing, B. and J.J. Pignatello, 1997: Dual-mode sorption of low-polarity compounds in glassy poly (vinyl chloride) and soil organic matter. Environ. Sci. Technol. 31, 792–799.

Yamamoto, T., Y. Noma, S.-I. Sakai, and Y. Shibata, 2007: Photodegradation of perfluorooctane sulfonate by UV irradiation in water and alkaline 2-propanol. Environ. Sci. Technol. 41, 5660–5665.

Yamashita, N., S. Taniyasu, G. Petrick, S. Wei, T. Gamo, P.K.S. Lam, and K. Kannan, 2008: Perfluorinated acids as novel chemical tracers of global circulation of ocean waters. Chemosphere 70, 1247–1255.

Yan, S., L.A. Rodenburg, J. Dachs, and S.J. Eisenreich, 2008: Seasonal air–water exchange fluxes of polychlorinated biphenyls in the Hudson River estuary. Environ. Pollut. 152, 443–452.

Zhang, L. and R. Lohmann, 2010: Cycling of PCBs and HCB in the surface ocean-lower atmosphere of the open pacific. Environ. Sci. Technol. 44(10):3832–3838.

Zhulidov, A.V., J.V. Headley, D.F. Pavlov, R.D. Robarts, L.G. Korotova, Y.Y. Vinnikov, and O.V. Zhulidova, 2000: Riverine fluxes of the persistent organochlorine pesticides hexachlorcyclohexane and DDT in the Russian Federation. Chemosphere 41, 829–841.