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Executive Summary

Concentrations of persistent organic pollutants (POPs) in air and water do show a remarkable spatial and temporal variability. Part of this variability is obviously associated to proximity to sources. On the other hand; there are a myriad of processes and variables in the biosphere that drive variability of POP concentrations in the environment. In fact, these processes can lead to change of concentrations of more than one order of magnitude. When assessing the risk associated to POPs, and their role as a driver of changes in ecosystems, it is important to have the information available on the sources of this variability, and the kind of variability they produce (seasonal, pulse, diurnal, spatial trends, vertical profiles, etc). Therefore the objective of this deliverable is to provide a review of the different kind of variability that has been found in the environment and comment on the potential processes driving this variability.

For temporal variability, and since POPs are semi-volatile organic compounds, temperature is identified as an important driver of atmospheric concentrations due to its influence on air-water partitioning. Furthermore there is an important variability at daily and diurnal scale due to several factors, such varying air masses, influence of carbon cycle on dissolved-phase POP concentrations etc. However, it is shown, that an important fraction of this variability at short time is currently not well understood. State of the art models, however, show that atmospheric inputs can induce ten-fold variability in POP concentrations in surface waters.

Concerning spatial variability, in addition to proximity to sources, there is also other variables that lead to an important spatial variability. Atmospheric sources such as diffusive uptakes and dry deposition are strongly enhanced at high wind speeds. Furthermore, since POPs are hydrophobic pollutants they can present a patchy distribution due to the influence of organic carbon cycle. Models for the European seas also show that there is a high variability in atmospheric inputs of POPs. The review of literature reported concentrations of PCBs, PAHs and PBDEs confirm this important variability

The identified spatio-temporal trends in POP concentrations and the identifications of some of the drives of these sources of variability provide important information that may eventually be useful in order to define the POPs impact that can lead to points of no return in ecosystems and identify thresholds.

1. Introduction

Concentrations of persistent organic pollutants (POPs) in air and water do show a remarkable spatial and temporal variability. Part of this variability is obviously associated to proximity to sources. For example, atmospheric concentrations are higher in urban areas than proximate waters (Brunciak et al. 2001, Dachs et al. 2002). However, the source of concentrations levels associated to primary inputs is usually easy to take into account in models, provided that sources are known and can be quantified.

On the other hand, there are a myriad of processes and variables in the biosphere that drive variability of POPs concentrations in the environment. In fact, these processes can lead to change of concentrations of more than one order of magnitude. When assessing the risk associated to POPs, and their role as a driver of changes in ecosystems, it is important to have the information available on the sources of this variability, and the kind of variability they produce (seasonal, pulse, diurnal, spatial trends, vertical profiles, etc). Therefore the objective of this deliverable is to provide a review of the different kind of variability that has been found in the environment and comment on the potential processes driving this variability. First, temporal variability will be reviewed, and in a second step, spatial patterns will be assessed. The rationale is to first look at longer scales, and from them to shorter (diurnal) scales. At the end of each section it is given a recommendation of the kind of variability (sinusoidal, pulse, etc) that should be used in modeling/experimental exercises for assessing the environmental impact of POPs.

2. Spatio-Temporal Variability of POPs

2.1. TEMPORAL VARIABILITY

2.1.1. Long term variability

Here, long term variability refers to changes in concentrations at the decadal scale. Unfortunately, there are very few long-term data sets available for persistent organic pollutants. Most of the information available for European water bodies comes from the reconstruction of historical registers from the analysis of sediment cores. These data sets show that there is a correlation of deposited material and historical emissions (Tolosa et al., 1995, 1996; Swarzenbach et al., 2003). For PCBs, for example, maximum levels in sediments are those that were deposited in the 60s and 70s, and concentrations have decreased during the last two decades (Tolosa et al., 1997). Conversely, for PAHs, historical records reflect the increase of deposited material since the industrialization of the 19th century (Fernández et al. 1999). On the other hand, “new” POPs show increasing concentrations during the last two decades.

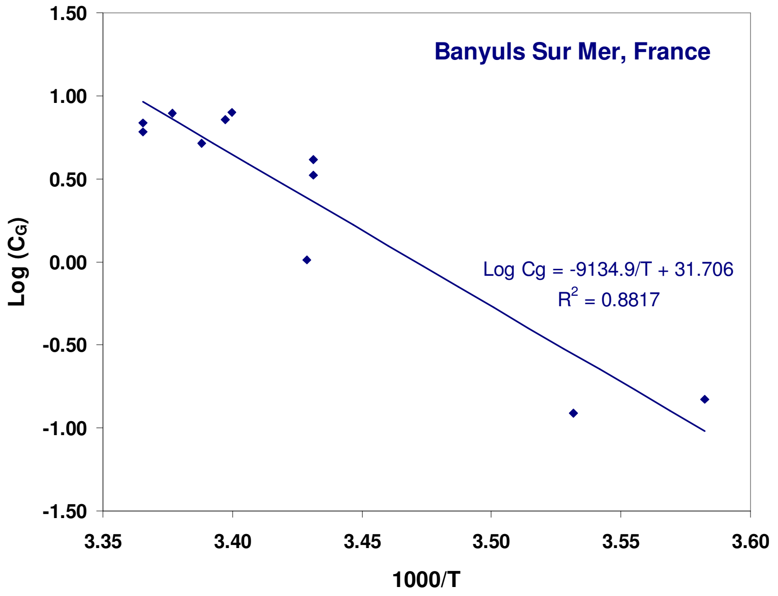
The long term trends are important since they provide information on how the biosphere process chemicals once they have been banned or are not used anymore. However, these long term trends as recorded in sediments do not show the levels to which the ecosystems are exposed, besides the benthic organisms, and do not show the variability at time scales shorter than a decade, in concentrations as a result of the myriad of environmental processes and sources that affect the spatial and temporal variability. In fact most of the temporal variability occurs at shorter time scales (seasonally to diurnally). Unfortunately, the factors that modulate this variability have not been comprehensively assessed so far, and a first attempt is done here.

In Models, the long term variability should be correlated to the emissions trends. For chemicals that were banned already, such as PCBs, then emissions are secondary from revolatilzation, and then the long term trends are more difficult to predict.

2.1.2. Seasonal variability

The seasonal variation of environmental concentrations of POPs may be the best known of all the variabilities occurring at different scales, especially for atmospheric pollutants. Indeed, gas-phase concentrations of most persistent pollutants, such as PCBs, are temperature dependent with higher concentrations during warm periods (Wania et al., 1998; Brunciak et al., 2001). This has been interpreted as the result of the importance of partitioning processes for semivolatile compounds such as POPs controlling the air-surface exchange and thus their atmospheric occurrence. Indeed, at higher temperature, the air-soil and air-water partition constants are higher, and thus a higher fraction of chemicals tend to be in the atmosphere. Conversely, at lower temperatures, the vapor pressure of the pollutant diminishes and it is favorable partitioned into condensed phases such as water bodies and soils. These trends have been observed ubiquitously in continental and coastal sites (Wania et al., 1998), but there is some evidence that over high seas this seasonality in gas-phase concentrations is not happening, even though these data sets are far from being comprehensive (Wania et al., 1998). These trends are ubiquitous and have also been reported elsewhere (Brunciak et al., 2001). The temperature dependence of gas phase concentrations is found for chemicals which occurrence in the environment is dominated by secondary sources, ie, environmental recycling through multicompartment partitioning. This is also the case of PBDEs and other priority pollutants of the European Union such as nonylphenols. Nonylphenols are an interesting case, since traditionally have been considered waterborne organic pollutants, even thought recent studies point out that they are ubiquitous in the European atmosphere. For example recent reports show that they occur in the North Sea and Mediterranean atmosphere (Ebinghaus et al., 2006; Dachs 2006). Seasonal data has been collected in Western Mediterranean in sampling sites of contrasting trophic status. This data shows that over the NE Mediterranean coastal atmosphere, gas-phase concentrations are temperature dependent (see Figure 2.1) with slopes (9130) similar to the few other reports of NP in coastal environments that is for the NE United States coast which resulted in a similar temperature dependence at the coastal site (slope of 8070) (Van Ry et al., 2000).

Figure 2.1. Temperature dependence of gas phase nonylphenols in the north-western Mediterranean Sea (Banguls sur Mer).



As commented above, these seasonal trends are due to the importance that air-water and air-soil exchange have as driving factors of atmospheric occurrence of POPs. However, the seasonal trends are not the same for those chemicals whose atmospheric occurrence is dominated by primary sources emitted directly to the atmosphere, as is the case for PAHs. There are quite a lot of contradictory assessments on the atmospheric seasonal variability of PAHs, especially for gas phase compounds. Conversely, for aerosol concentrations of PAHs, it is usually found that concentrations increase during winter months and decrease during summer. This has been interpreted as linked to the emissions trends since PAHs emissions from home heating are higher during winter. Furthermore, atmospheric degradation of PAHs is higher during the summer due to higher OH concentrations and higher reaction rates, therefore, this decreases gas-phase concentrations of atmospheric PAHs during warm periods.

The data available on water column seasonal variability in terms of POP concentrations is scarce and the factors driving it largely unknown. Sobek et al. (2004) has shown that particulate concentrations vary with maximum concentrations in winter that are 100 fold those in the early summer, at least in the Baltic. The variability was a factor of 30 for dissolved phase PAHs. However, this extreme variability has not been observed in other environments, and may be related to sediment resuspension events modifying substantially water column concentrations (Bogdan et al. 2002; Jurado et al. 2006).

Therefore, for the atmospheric environments and for most POPs, the seasonal trends follow a clear seasonality that is correlated with the temperature, with higher concentrations by late spring, early summer. For some chemicals such as PAHs, the variability is quite more difficult to model and environmental degradation processes, seasonal trends in emission, etc should be taken into account.

2.1.3. Short term (daily) variability

Short term variability is referred to the variation in environmental concentrations of POPs at scales of few days; this is specially observed in the atmospheric environment. It is well known that short term variability does not occur in some environmental matrixes, specially sediments and soils. This is due to the fact that the reservoir capacity of soils and sediments to accumulate POPs is so large (Dalla Valle et al., 2005) that the output or input fluxes in a week time can not vary the inventory in that phase. In aquatic environments, the reservoir capacity of the surface ocean is usually higher than that of the lower atmosphere (Jurado et al., 2004). Therefore, the short term variability will be observed mainly in the atmosphere.

As commented above, temperature is an important factor driving the occurrence of PCBs in the gas phase, and part of the daily variability, which can be as high as a factor of 3-5 can be explained by temperature changes (Brunciak et al., 2001; Giglioti et al., 2000). However, on the short term, the back trajectory of the air mass, and the variability associated to this seems to be more important. Indeed, several authors have observed that high concentrations are associated to POPs from certain directions, usually with urban/industrial regions upstream (Van Droodge et al., 2002). Therefore, the short term or daily variability seems to be correlated with the spatial variability of POP concentrations in the upstream region of the air-masses (Dachs et al., 2002).

Again, reports on the short term variability of water column concentrations of POPs are scarce. Garcia Flor et al (2005) has shown that daily variability of dissolved and particulate PCBs concentrations in Western Mediterranean coastal sites have a variability of a factor of 2-3, part of it related to organic carbon content variability. This is not only true for PCBs concentrations in the water column, but also for those chemicals found in the surface microlayer. This range of variability is similar to that shown by Guitart et al. for PAHs in the same environments (Guitart et al., 2004). It is difficult to infer daily variability from other studies because usually daily variability is masked by spatial variability.

The short term variability is the most difficult to model, if the location of the sources is known, higher concentrations should be modeled when the air-masses are from those directions. However, with the present status of knowledge, modeling efforts should include a stochastic signal around an average values (as those reported in Annex A).

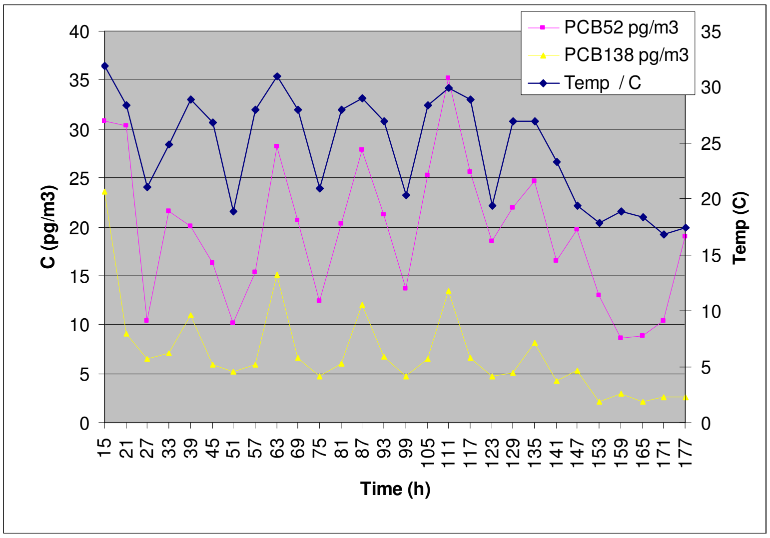
2.1.4. Diurnal variability

Diurnal variability has not been traditionally studied in detail, but during the last years, there have been an increasing number of reports showing that this is an important component of the fate of POPs. This variability, in some cases, can be driven by atmospheric processes and/or biogeochemical processes in the water column. As it happens again for the daily variability, this kind of variability can only be observed for POPs in the atmosphere and water column, even though, so far has only been described by the atmosphere. Nevertheless, there is evidence that it also happens in the water column is discussed below.

The diurnal cycle of organic pollutants in urban atmospheres is the result of the emission pattern and atmospheric degradation processes. Dachs et al. (2002) has shown that PAHs atmospheric concentrations are higher during periods of high traffic intensity with minima at night (due to a lack of emissions), and at midday due enhanced degradation due to OH attack. This urban contamination, does influence the levels and atmospheric deposition of pollutants down wind (Perez et al., 2003; Simcik et al., 1997).

For other coastal environments, not urbanized but forested or dominated by vegetation, it has been shown, that air contamination over vegetation also follows a diurnal cycle with higher concentration during the day due to higher temperatures (Lee et al., 1998). This has been observed for PCBs, PAHs and PBDEs (Hornbuckle et al., 1996; Gouin et al., 2002).

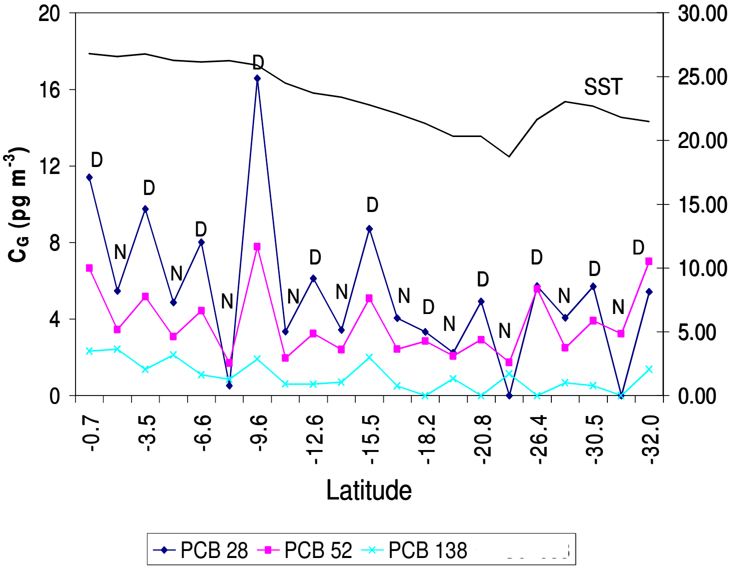
Figure 2.2. Diurnal variability of PCBs as function of temperature (from Lee et al., 1998).



In the coastal zone, sea breeze does play an important role modulating the diurnal variability and fluxes of pollutants. Perez et al. (2003) has shown that changes of concentrations do occur and are related to different wind directions. Furthermore, the air-sea exchange of pollutants follows the pattern of wind speed intensity, with 80% of the daily flux occurring during the sea-breeze periods. Unfortunately, this is the only report available on this important process which may be important for the European seas. In addition, sea breezes are an important mechanism for the transfer of pollutants between the coastal seas and the continents.

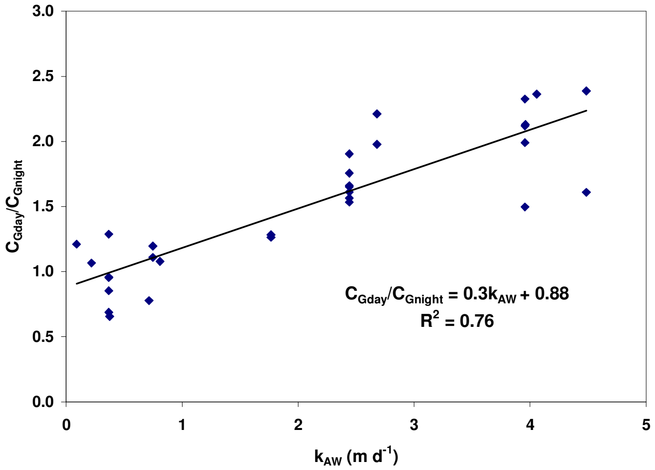
Over other European marine waters, it has been shown that gas phase concentrations of PCBs are also modified by the oxidizing potential of the atmosphere. Mandalakis et al. (2003) have shown that gas phase concentrations of PCBs during the day can be depleted significantly due to oxidative attack of OH radicals. These changes in gas-phase concentrations should drive a change in the air-water equilibrium, and thus water side concentrations. However, there is not a single report in the literature on this.

Figure 2.3. Diurnal cycle of gas phase concentrations of PCBs over the NE Atlantic Ocean at different latitudes. SST is the sea surface temperature (from Jaward et al., 2004)



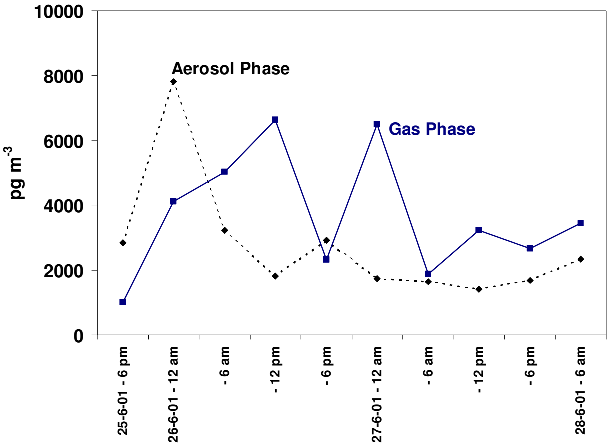
Especially important is the recent work by Jaward et al. (2004), who observed a consistent diurnal cycle of PCB and PAH concentrations in the atmosphere over the tropical Atlantic (see Figure 2.3). Jaward et al. (2004) reviewed all the potential causes that could lead to this variability in the atmosphere, but they were not able to identify a single atmospheric process that could lead to these trends. This trend is only apparent for the more volatile compounds, but not for the less volatile. In fact, it is possible to plot the magnitude of the diurnal cycle versus the Henry Law’s constant (Figure 2.4). This suggests that air water exchange is modulating the magnitude of the cycle in gas phase concentrations, and provides evidence that there is, as well, an important cycle in the dissolved phase concentrations. Again, Jaward et al. (2004) reviewed the potential processes driving this variability, and they concluded that it was a constellation of processes affecting the organic carbon cycle, such as bacterial reworking, cycle of DOC, zooplankton diurnal migration, etc.

Figure 2.4. Extend of the diurnal cycle (C_{day}/C_{night}) versus Henry's Law constant (Jaward et al. 2004).



Some recent data from the Mediterranean Sea, specifically the Alboran Sea suggests that there is also an important variability in this coastal atmosphere (see figure 2.5). However, in this case, the diurnal cycles are not only the result of what is occurring in the water column, but also of different air masses affecting the sampling site.

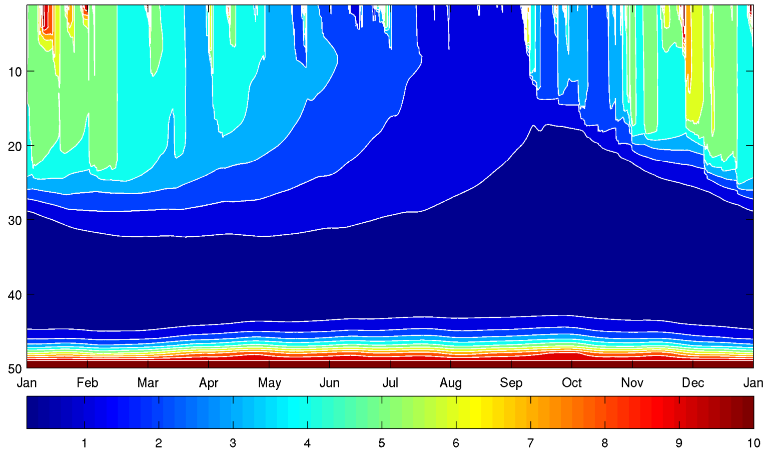
Figure 2.5. Diurnal variability of PAHs in the SW Mediterranean (Alboran Sea).



Therefore, it is now clear that there is an important variability occurring at the diurnal time scale, but the processes that control this variation in atmospheric and water concentrations are largely unknown.

In models, the diurnal variability should follow the trends of temperature for continental ecosystems, but for the marine environments, the current knowledge does not allow to provide a general trend for all ecosystems, even though the best approach would be sinusoidal function around the values reported in Annex A.

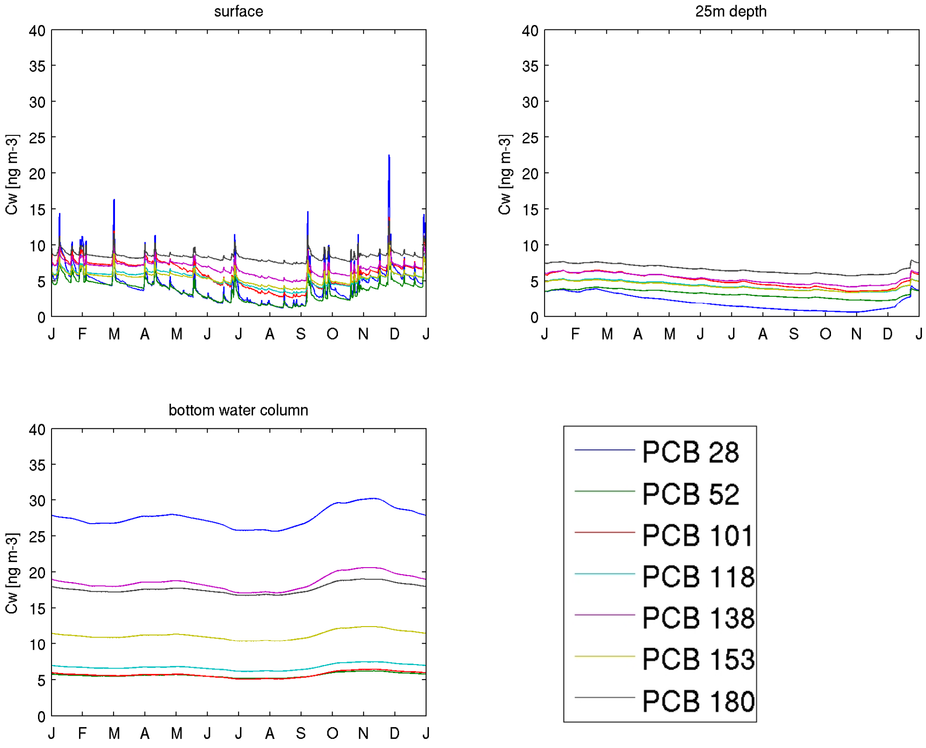
Figure 2.6. Seasonal and daily variability in the vertical profile of PCB 28 for a coastal water column of 50 m depth.



2.1.5. What models tell us about temporal variability?

Within the Thresholds project, a fate and transport model for POPs in the water column has been developed. This model is able to predict the vertical profiles and their daily and seasonal variability. Figure 2.6 shows the seasonal variability in the vertical profiles for a PCB congener when the water column is 50 m depth. It is possible to distinguish three zones. Deep water shows a huge influence from the sediment, mainly due to sediment resuspension and diffusion of chemicals from the interstitial waters to the deep waters. Conversely, the surface waters are extremely sensible to atmospheric inputs with pulses of concentrations due to atmospheric deposition. The layer in the mid-depth water has low concentrations and reasonably constant all year round. This different variability in water concentrations of PCBs is depicted in Figure 2.7, which clearly shows that variability can be ten fold in surface waters, while sediment concentrations remain close to a constant value around all year. Therefore, models allow to obtain a picture on the temporal variability of POPs that otherwise would be impossible to assess due to limitations in the number of samples that can be analyzed in any field study.

Figure 2.7. Variability in water concentrations of different PCB congeners at three different depths for a typical year and a water column of 50 m.



2.2. SPATIAL VARIABILITY

Most reports on POPs in marine environments do intrinsically deal with the spatial variability of their concentrations. However, few times the patterns governing the variability are discussed in detail, and sometimes this spatial variability is masked by the temporal variability. Here, there is a summary of the knowledge available on the spatial variability of POPs in aquatic environments. The intention is not review the variability for each one of the European marine regions, but to provide the general trends that follow pollutants in most basins. This assessment is done at different scales. Furthermore, Annex A provides a literature review of the concentrations in the different media for PCBs, PAHs, and PBDEs. This data set compiled from the literature, shows that there is a considerable variability in environmental concentrations of POPs. Therefore, the impact of these can also be different for different environments depending these values are above or not a certain threshold.

2.2.1. Regional scale

Here, variability at regional scale is that occurring in the meso-scales, from tens to hundreds of kilometers. In sediments, the variability is dominated by two processes. The highest concentrations are usually closer to sources (Tolosa et al., 1995, 1997; Lipiatou et al. 1997). These sources can be either those regions close to urban centers, or those regions receiving sedimentary inputs from rivers. For example, in the North-western Mediterranean region, Salau et al. (1998) have been able to show that significant higher concentrations of PCBs and PAHs are found near Barcelona, and near the Ebro and Rhone river mouths. Similar trends can be found in the Black sea, with the influence of the Danube, and in other basins (Maldonado et al., 1999). Out of the continental margins, variability in POPs concentrations in sediments is much lower and this is very much related to the variability of organic carbon in the sediments. This is true for most POPs, except for those that are mainly associated to soot carbon, for these, the spatial variability at open sea is correlated to the spatial availability of soot carbon (Gustaffson et al., 1997). This relationship of PAHs and soot carbon is related to the introduction of POPs in the open sea due to atmospheric deposition. In addition, Gustafsson (1997b) has also shown that vertical fluxes of PAH in the water column are correlated to distance from sources. For other POPs, the transfer to deep waters and sediments is favored by the biological pump where part of the pollutants sorbed from surface waters sink to the deep oceans (Dachs et al., 2002). The spatio-temporal variability of vertical fluxes of OC and associated POPs is quite patchiness and difficult to predict (Dachs et al., 1996; Bouloubassi et al., 2006).

The causes of the regional variability of POPs in the water column are much more difficult to identify, but with the exception of coastal zones, where they are related to proximity to sources, are very much linked to the carbon cycle. Indeed, particulate concentrations of POPs such as PCBs and PAHs follow in great measure the spatial variability of phytoplankton biomass (Dachs et al., 1997a,b; Sobek et al., 2004), and particulate organic carbon in general. This has been observed in the Mediterranean (Dachs et al., 1997a,b), Black Sea (Maldonado et al., 1999), North Sea (Xie et al., 2006), Baltic sea (Bruhn et al., 2003). Still, not all the variability can be explained by the amount of organic carbon, but there are a number of questions that need to be answered about the role of vertical mixing (Jurado et al., 2006), zooplankton (Berrojalbiz et al., 2006), and the microbial loop (Wallberg et al., 2000) controlling the occurrence of POPs in the water column, which need further research.

2.2.2. Vertical Variability

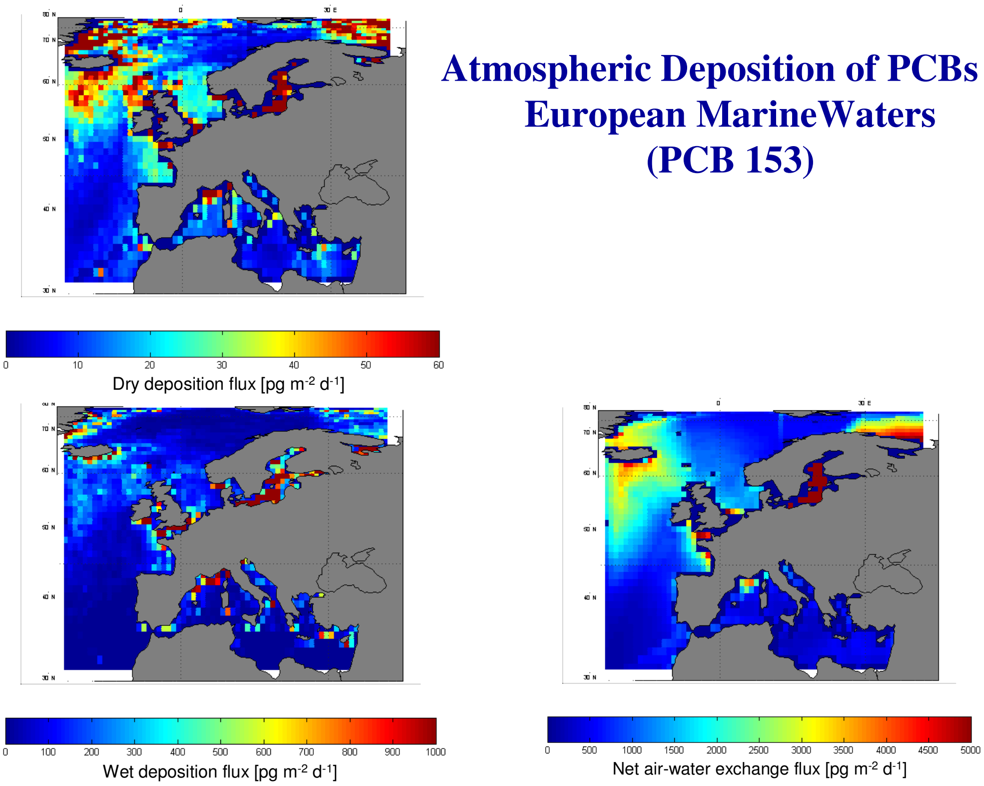
The vertical profiles of POPs show consistently higher concentrations in surface waters than at deep waters. These surface enriched-depth depleted vertical profiles are the result of: i) introduction of POPs in surface waters, ii) POP follow the vertical profile of organic carbon with enrichment at the phytoplankton biomass, iii) POPs are transferred mainly to deep waters by association to settling particles (Dachs et al., 1997a,b, Shulz bull et al., 1998).

In addition to the enrichment in surface waters, in some locations it has been found that POP concentrations increase near the sediment (Dachs et al., 1997; Bogdan et al,. 2002), and this is related to the influence of sediment resuspension and diffusion from the sediment as demonstrated recently from models.

2.2.3. What models tell us about spatial variability?

The modeling efforts so far have dealt mainly on assessing how spatial variability of atmospheric deposition influences the water column concentrations and sinks. The applications of the recent methodology developed by Jurado et al. (2004, 2005) to European waters allows to identify the regions receiving higher concentrations of POPs from the atmosphere (see Figure 2.8). From this picture, it is clear that there is a considerable variability that comes from the important variation of atmospheric POPs concentrations. Furthermore, wet deposition is an important source of variability at regional scale, as well as at temporal scale as seen before. The geographical variability, in addition to influenced by atmospheric concentrations of POPs, it also depends to a great extend to the precipitation events, wind speed average and variability, atmospheric stability etc. In any case, the results shown in Figure 2.8 indicate that there is an important variability at the European scale that is sometimes higher than one order of magnitude in terms of the atmospheric inputs.

Figure 2.8. Diffusive air-water exchange, dry aerosol deposition and wet deposition of PCB 153 for the European Seas.



3. Conclusions

The revision of the observed spatio-temporal trends and patterns of POPs in the environment allow identifying sources of variability and their magnitude. This is important, because, the reported concentrations found in many studies may not be representative of the pressures to the ecosystems.

- The variability is small for long term temporal trends, but increasingly higher at short time scales. At daily-diurnal scales it can be of a factor of ten.
- Models shown that atmospheric inputs of pollutants can lead to a high variability in POP concentrations in aquatic environments
- Proximity to sources is an important driver of spatial variability in POP concentrations, as expected.
- Environmental conditions (temperature, wind speed) and trophic status are also important drivers of environmental variability of POPs.
- Models show that European seas are subject to important atmospheric inputs of POPs, but that these do vary in a great measure depending on a number of factors.
- The review of published assessments of environmental concentrations show that there is as well, as predicted, an important regional variability in PCBs, PAHs and PBDEs concentrations. The sources of this variability are not always understood.
- The patterns of variability identified here, together with the known and reported environmental concentrations will allow to study, in conjunction with models, the potential impact of POPs in Ecosystems in order to identify Thresholds.

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ANNEX A: Environmental Concentrations of PAHs, PCBs & PBDEs

A.1. PAHs

A1.1.1 Water

Individual PAHs Concentrations

Table 1 - PAH concentration (pg/L) in the North Atlantic and Mediterranean water columns (Lipiatou *et al.* 1997).

Compound	Mediterranean Sea		North Atlantic	
	Dissolved	Particulate	Dissolved	Particulate
Phenanthrene	240	170	400	1.8
Fluoranthrene	350	40	110	1.9
Pyrene	67	28	74	1.3
Benzo(a)anthracene	10	3	6	0.5
Chrysene+triphenylene	7	7	2	1.8
Benzofluoranthenes	14	15	7.5	2.5
Benzo(e)pyrene	24	0.5	1.6	0.5
Benzo(a)pyrene	7	0.7	1.5	0.5
Benzo(ghi)perylene	0.5	1.9	0.4	0.5
Indenol(1,2,3-cd)pyrene	0.5	1.7	0.4	0.5

Table 2 - Maximum concentration (ng/L) of several PAHs in different locations (Hellou *et al*., 2005).

Location	Phenanthrene	Fluoranthene	Pyrene	phase
Iceland/North Atlantic	0.03	0.009	0.007	Dissolved
Norway, reference site	9.9	120	33	D
Chesapeak bay	4.1	22.1	10.6	D
England and Wales	2130	313	205	D
Norway, sewage effluent	1117	515	248	D
Halifax harbor	0.643	5.717	2.876	D
Baltic sea	1.310	3.930	2.00	D+ particulate
Greece seawater	58	37	50	D+ particulate
Greece sewage effluent	1987	452	1371	D+ particulate
Greece waste water	900	100	167	D+ particulate
Montreal, influents	333	150	138	D+ particulate

Total PAH Concentrations

Table 3 - Summary of total PAH concentration, maximum, in sub-surface water from various sites in the world (Zhang *et al.* 2004 and Hellou *et al.,* 2005).

Location	ng/L
Eastern Mediterranean	0.489
Baltic sea	0.594
Chesapeake bay, USA	65.7
Halifax harbour, USA	250

Danube estuary	0.214
Seawater around England and Wales	24821
Seine river and estuary	36
Northern Greece	856
Western Xiamen sea, China	945

A1.1.2 Sediment

Individual PAHs Concentrations

Table 4 - Sediment concentration, maximum, (ng/g) from different water depths - Alborean sea (southwestern Mediterranean) (Dachs *et al.* 1996).

PAHs	**250 m**	**500 m**	**750 m**
Phenanthrene	230	225	275
Methylphenanthrene	160	175	210
Dimethylphenanthrenes	150	115	120
Anthracene	20	15	25
Dibenzothiopene	100	90	140
Methyldibenzothiophenes	145	125	145
Dimethyldibenzothiophenes	210	90	100
Fluoranthene	45	60	75
Pyrene	70	100	125
Benzo(a)anthracene	20	20	18
Chrysene	50	40	38
Total benzofluoranthene isomers	55	50	45
Benzo(e)pyrene	35	30	25
Benzo(a)pyrene	25	25	15
Perylene	15	15	10

Table 4 - PAH distribution, maximum, in surficial sediments (ng/g) of western Mediterranean Sea (Lipiatou *et al.,* 1997).

	Rhone Delta	Ebro Delta	Gulf of Lions	Balearic Sea	Open Sea	Open Sea
Phenanthrene	180	6	65	25	20	10
Anthracene	25	2.5	2	8	2	2.5
Fluoranthrene	150	16	45	55	22.5	17.5
Pyrene	125	17.5	32	45	12.5	12
B(a)anthracene	75	7.5	15	25	10	7.5
Chrysene	100	12.5	35	50	25	17.5
Benzofluorene	200	22	45	130	39	16
Benzo(e)pyrene	75	10	15	45	19	7.5
Benzo(a)pyrene	100	7.5	12.5	35	9	3.5
Indenopyrene	75	6.5	-	55	10	12.5
Benzo(ghi)perylene	100	8	7.5	50	11	11

Table 5 - PAH concentration, maximum, of 16 parent PAHs for sediments of the Niger Delta, Nigeria (Olajaire *et al.*, 2005).

PAH	**ng/g dw**
Naphthalene	8.92
Acenaphthylene	1.76
Acenaphthene	6.71
Fluorene	7.27
Phenanthrene	16.86
Anthracene	5.98
Fluoranthene	5.00
Pyrene	3.80
Benzo(a)anthracene	1.81
Chrysene	2.66
Benzo(b)fluoranthene	2.57
Benzo(k)fluoranthene	2.32
Benzo(a)pyrene	1.31
Dibenzo(a,h)anthracene	0.4
Benzo(g,h,i)perylene	2.08
Indeno(1,2,3-cd)pyrene	1.11

Table 6 - Concentration (ng/g dw) sediment, Ariake Sea (Nakata *et al.,* 2003)

PAHs	**Tidal flat**	**Coastal water**
Anthracene	4.4	<0.02
Chrysene	16	<0.02
Benzo(a)anthracene	19	<0.2
Benzo(b)fluoranthene	39	<0.05
Benzo(k)fluoranthene	16	<0.02
Benzo(a)pyrene	20	<0.03
Indeno(1,2,3-cd)pyrene	23	<0.2

Total PAHs Concentrations

Table 7 - Summary of PAH concentration (maximum) in sediments from various sites in the world (Zhang *et al.* 2004 and Qiao *et al.,* 2005).

Location	**ng/g dw**
Casco bay, USA	20748
Chesapeake bay, USA	180
England and Wales	102471
Kitimat harbour, Canada	528000
Kyenoggi bay, Japan	1400
Masan bay, Korea	1100
Penobscot bay, USA	8800
San Diego bay, USA	20000
San Francisco bay, USA	27680
Todos santos bay, Mexico	813
Victoria Harbour, Hong Kong	26100
Western Xiamen sea China	33000

Jiulong river estuary, China	1177
Pearl river delta, China	10811
Bohai sea and the yellow sea, China	5534
Yangtze estuary, China	11740
Western Baltic sea	30100
Northwestern Black sea	269
Humber plume, North sea	1700
Kara sea and adjacent rivers, Russia	810
River Tonghui, Beijing, China	928
Minjiang river estuary, China	877
Guba Pechenga, Barents sea, Russia	208
Yalujiang River, China	1500
Deep bay, China	726
Minjiang River Estuary, China	887
Lingding Bay, China	1006
Bohai Sea, the yellow sea, China	5734
Zhujiang River, China	10811
Izmit Bay, Turkey	25000
Kiel Harbour	30000
Meilang Bay, Taihu Lake	4754

Table 8 – Data from Lipiatou *et al.* (1997), total PAH concentration in Mediterranean surficial sediments.

Area	**ng/g**	**Water depth, m**
Northwestern Mediterranean	620,750	2500,1700
Coastal shelf between Monaco and Rhone Delta	128-238	-
Rhone Delta	376-1878	10-80
Rhone Delta	1225-2457	23-90
Western Mediterranean central cyclonic gyre	179	2970
Rhibe Delta	1070-6364	4-95
Ebro Delta	200-6500	10-1000
Ebro Delta	50-170	30-50
Ligurian Sea off Monaco	599-723	250
Adriatic Sea	12-174	29-252
French Riviera-Marseilles	103-1582	-
French Riviera-Toulon	912-8525	-
French Riviera-Cannes	393-661	-
West Coast-Corsica	3.5-54	-
Gulf of Lions	182-763	69-2200
Gulf of Lions shelf, slope, fan	470-590	80-1500
Balearic/Catalan sea	100-500	1000-1500
Coastal area near urban centres of Barcelona and Valencia	1396-2313	10-25

In unpolluted coastal area PAHs occur at concentrations up to 1 μg/g.

A1.1.3 Water and Sediment

Individual PAHs Concentrations

Table 9 - Concentrations (maximum) in water and lake sediments of Lac Saint Louis (Mackay and Hickie, 2000).

PAH	Water ng/l	Sediments ng/g dw
Anthracene	0.6	5
Benzo(a)pyrene	0.48	43
Chrysene	1.2	43
Fluoranthene	4.1	46
Phenanthrene	8.1	15
Pyrene	3.1	24
Benzo(a)fluoranthene	4.2	91

Table 10 - PAH concentrations (maximum) in Ninjiang river estuary, China (Zhang *et al*., 2004).

PAH	Water (µg/L)	Pore water (µg/l)	Sediment (ng/g)
Naphthalene	1.2	2.3	11.2
Acenaphthylene	1.4	12.5	19.7
Acenaphthene	1.4	1.6	16.3
Fluorene	1.6	2.7	16.0
Phenanthrene	6.1	2.3	8.5
Anthracene	1.9	2.6	11.2
Fluoranthene	4.4	2.3	46.8
Pyrene	3.3	1.6	52.5
Benzo(a)anthracene	2.0	3.7	168
Chrysene	4.5	10.2	115
Benzo(b)fluoranthene	138	31.6	55.1
Benzo(k)fluoranthene	4.3	36.2	258
Benzo(a)pyrene	166	30.4	88.0
Indeno(1,2,3-cd)pyrene	126	36.9	96.6
Dibenzo(a,h)anthracene	40.2	30.2	368
Benzo(g,h,i)perylene	11.9	47.5	65.5

A1.2. PCBs

PBC-126 is environmentally relevant (Wassenberg and di Giulio, 2004).

A1.2.1 Water

Individual PCBs Concentrations

Table 11 - Volumetric concentrations of individual PCB congeners expressed as pg/L at the three different depths (Axelman *et al.*, 2000).

PCB	**12 m**	**40 m**	**91 m**
Particle bound			
52	0.25	0.4	0.2
101	0.6	0.7	0.8
118	0.4	0.5	0.4
153	1..1	2	0.8
105	0.1	0.25	0.2
138	4	5	2
180	3.5	5	0.7
Dissolved			
52	7.5	9	3
101	7.5	10	4
118	2	4	0.75
153	5	7	2
105	0.7	0.9	0.3
138	5	8	1
180	1.2	5	0.9

Table 12 - Barent Sea (Artic Sea) water PCBs (maximum) concentration (Borga and di Guardo, 2005).

PCB	Water (pg/L)
28	0.24
52	0.24
101	0.17
105	0.06
110	0.12
118	0.18
138	0.26
149	0.0
153	0.09
180	0.21

Total PCBs Concentrations

Table 13 - Concentration levels (maximum) of PCBs in water samples from Western Mediterranean (Tolosa *et al.*, 1997).

	Water phase	Conc ng/L	Compound
Estuarine			
Rhone	Bulk sample	38	
Ebro	Dissolved	0.64 2.4	Aroclor 1260 Aroclor 1254
Ebro	Particulate	2.7 3.9	Aroclor 1260 Aroclor 1254
Var	Dissolved	1.75	Aroclor 1254

Var	Particulate	2.6	Aroclor 1254
Coastal			
French coast (Marseille)	Bulk sample	0.002	1254
Sete-Monaco	Bulk sample	29	Phenochlor DP.5
Monaco	Microlayer	42	1254
Monaco	Dissolved	<0.5	1254
Monaco	Particulate	1.1	1254
Languedoc-Provence-Cote Azur	Bulk sample	<2	Phenochlor DP 5/6
Corsica	Bulk sample	<2	Phenochlor DP 5/6
Barcelona	Dissolved	0.06	Σ28,52,101,118,138,180
Barcelona	Particulate	0.17	Clophen 60
Ebro	particulate	0.035	Clophen 60
Open Sea			
Western Basin	Bulk sample	4.5	Phenochlor DP 5/6
Liguro-Provencal (surface)	Dissolved	1.9	Aroclor 1254
Liguro-Provencal (surface)	Particulate	4.6	Aroclor 1254
Liguro-Provencal (profile)	Dissolved	13.4	Aroclor 1254
Liguro-Provencal (profile)	Particulate	17.7	Aroclor 1254
Liguro-Provencal (basin)	Bulk sample	<2	Phenochlor DP 5/6
Western basin	Bulk sample	0.024	Kanechlors300,400,500, 600
Catalan sea (profile)	Particulate		Clophen 60
Catalan Sea	Dissolved	0.05	Σ28,52,101,118,138,180

A1.2.2 Sediment

Individual PCBs Concentrations

Table 14 - Sediment concentration, maximum, (ng/g) from different water depths (Alborean sea) (Dachs *et al.,* 1996).

PCB	**250 m**	**500 m**	**750 m**
28	1.5	2	2.85
52	2.5	2.60	4.2
101	0.9	2	3.1
118	2.2	1.9	2.9
153	2.6	1.9	3.8
138	1.85	1.75	2.6
180	1.5	1.0	1.5

Table 15 - Maximum concentrations (ng/g dw) in sediments of the Ariake Sea (Nakata *et al.,* 2003).

PCB	**Tidal flat**	**Coastal water**
105	0.1	0.96
118	0.51	2.6
156	<0.05	0.18
77	0.009	-
126	<0.01	-
16	<0.01	-

Table 16 - Sediment cores PCBs from the Baltic proper and Gulf of Finland (Jonsson , 2000).

PCB	**ng/g dw**
167 (Bornholm basin)	15
169 (Gdansk bay)	15
170 (Lithuania)	22
171 (East Gotland deep)	59
178 (West Gotland Deep)	47
180 (N. Baltic Proper)	95
182 (Central Gulf of Finland)	12
187 (Inner gulf of Finland)	18

Table 17 - PCBs in Singapore's coastal marine sediments, maximum concentrations (Wurl and Obbard, 2005).

PCB	**ng/g dw**
28	31.9
31	8.9
33	14.3
44	13.3
49	10.7
53	11.2
70	13.3
74	13.9
87	13.3
118	13.6
128	13.1
138	13.9
153	21.9
206+208	41

Table 18 - Maximum concentrations of dioxin like-PCBs in coastal sediments (pg/g dw) (Eljarrat *et al.*, 2005).

PCB	**pg/g dw**
81	50.8
77	193
126	25.9
169	9.26
105	4065
114	320
118	5442
123	1159
156	2149
157	173
167	233
189	179

Table 19 - Concentration, maximum, of PCBs in Baltic sediments (ng/g dw) several depths (0-2 cm) (Konat and Kowalewska, 2001).

PCB	**ng/g dw**
28	56.2
52	28.54
101	28.74
118	16.19
153	13.01
138	9.96
180	11.93

Total PCBs concentrations

Table 20 - PCB laminated cores (ng/g dw), from offshore and archipelago areas of the NW Baltic sea (Jonsson *et al*., 2000).

	NW Baltic proper	N Baltic Proper	S Baltic Proper	NE gulf of Finland
PCBs	20	39	2.4	60

Table 21 - Maximum concentrations of PCBs in surface sediments of various marine environments-literature data (Konat and Kowalewska, 2001 and Tolosa *et al.,* 1997).

Area (n. PCBs)	**ng/g dw**
Baltic	
Gulf of Bothnia (12)	6.5
Baltic proper(12)	11.0
Arkona basin (23)	5.4
Oder river estuarine (23)	26.3
North Sea	
Humber Plume (12)	19.7
Scheldt Estuary (13)	200
Mediterranean Coast	
Tunisian coast	0.5
Coast of Alicante (10)	2.9
Coast of France	15850
Coast of Greece	775
Italian coast	3200
Rhone Estuary-Fos Gulf	416
Gulf of Lions	780
Nice	1165
Monaco	61
Central Tyrrehian coast	410
Continental shelf Ebro	6
Barcelona	483
Tarragona	122
Valencia Coast	25
Tiber estuary	770
Tiber offshore	73

Naples bay	3200
Naples offshore	170
Sicily	82
Tunisian Sea	1.1
Algerian Sea	323
Open sea	
Alguero-provencal Basin	9
Liguro-Provencal basin	33
Tyrrhenian Sea	1.3
Gibraltar sill and Sicilian –Tunisian sill	0.8
Adriatic	
Venice Lagoon	185
Venice coastal	2203
Venice gulf	9.69
Open sea	332
Atlantic Ocean	
Dominican coast (21)	41.9
Artic ocean	
Chucki Sea	0.14
Pacific Ocean	
Gulf of Alaska	2
Bering sea	0.13
Coastal USA	1000
South China Sea	
Hong Kong	9.75 (wet weight)
Canadian lakes	39

Table 22 - Sediment PCBs concentration, maximum, in Wurl and Obbard, 2005.

PCB	**ng/g dw**
Osaka Bay, Japan	24.0
Hong-Kong	97.9
Masan bay Korea	41.4
North coast of Vietnam	66.4
Minjiang river estuary, China	57.9
Daya bay, China	11.2
Yangtze Estuary, China	19.0
Singapore	32.9

In Spanish coastal sediments Eljarrat *et al.* (2005) reported a concentration between 0.3 and 75 pg/g dw.

In Swedish lakes (Insjon and Lunsjon) PCBs concentration in the sediment was reported to be 17 ng/g (Soderstrom *et al.*, 2000).

In the USA, PCBs (1, 2, 13, 4, 6, 8, 9, 16, 18, 19, 22, 25, 28 ,52, 44, 56, 66, 67, 71, 74, 82, 87, 99, 110, 138,1 46, 147, 153, 173, 174, 177, 179, 187, 180, 194 ,195, 199, 203, 206) in Lake Michigan, surficial sediments was 40 ng/g dw and in Lake Huron 20 ng/g dw (Song *et al.,* 2005).

A1.2.3 Water and Sediment

Individual PCBs Concentrations

Table 23 - Lake Ontario PCBs maximum concentrations (Oliver and Niimi, 1988).

PCB	Water pg/L	n/g dry weight Bottom sediment	ng/g dry weight Bottom sediment
8	18		
28+31	46	17	
18	72	4.3	
22	6.7	2.0	
16	3.4		
26		0.1	
33	14	0.5	
17	9.7	0.5	
25		0.4	0.3
24+27		0.4	0.2
32	1.4	0.6	1
66	31	46	27
70+76	45	23	25
56+60+80	26	33	19
52	63	25	15
47+48	41	12	3.4
44	50	23	12
74	10	2.7	4.6
49	24	11	5.8
64	9.7	9.4	4.0
42	3.7	4.7	2.6
53	5.9	0.5	0.5
40	6.2	3.1	1.4
41+71			0.8
46		0.7	0.3
45		1.1	0.2
101	130	27	19
84	19	21	15
118	34	15	21
110	55	37	25
87+97	26	20	17
105	14	10	12
95	52	14	12
85	14	9.8	5.6
92	14	9.1	6.9
82	4.7	2.9	2
91	40	5.7	3.6
99	14	7.2	4.7
153	50	25	23
138	28	15	15

149	34	20	14
146	7.3	6.7	3.4
141	8.6	7.4	5.1
128		4.9	6.2
151	2.7	307	1.7
132	45	11	6.6
156		2.1	2.3
136	16	0.7	2.1
129		1.4	0.8
180	27	13	13
187+182	18	8.4	7.8
170+190	7.2	10	8.4
183	4.4	3.1	3.8
177	3.0	2.5	3.6
174	3.2	4.1	3.7
178		1.7	1.2
171		1.9	2.2
185		1.0	0.5
173		1.6	0.4
203+196	6.8	8.2	6.8
201		7.2	5.7
194	7.8	3.7	3.7
195		1.2	1.7
205		1.6	1.3
206		4.8	4.2
207		1.0	0.4
209		9.4	7.6

Table 24 - PCB (maximum) concentrations in Minjiang River estuary, China (Zhang *et a*l., 2003).

PCB	**Surface water (ng/L)**	**Pore water (ng/L)**	**Sediment (ng/g dw)**
1	10.2	86.95	1.86
5	4.01	26.59	0.29
29	292.0	3605	1.14
28	404	1670	2.26
52	302..0	1324	11.91
49	91.32	666.1	10.92
47	155.0	639.9	8.33
97	165.0	750.4	1.87
101	117	352.3	2.66
154	480	1221	5.30
105	97.3	265.8	0.61
171	52.5	158.6	4.82
77	135	564.6	9.10
118	253.6	789.9	2.95
169	127.2	156.9	1.22
153	41.17	167.6	0.54
138	357	352.1	4.21
187	52.5	124.4	2.23
200	304	306.4	1.91
204	350	71.24	1.09
180	44.05	422.1	0.97

Total PCBs Concentrations

Table 25 - PCBs (maximum) concentrations at 3 different depths (three Swedish lakes) (Berglund *et al*., 2001).

Lake	1 cm ng/g dw	15 cm ng/g dw	22.5 cm ng/g dw	Water Dissolved ng/m3	Water particulate ng/m3
Sovdesjon	20	25	40	6	156
Finsjasjon	80	30	70	23	135
Mien	60	50	10	23	5

PCBs concentration varies with type of lake, eutrophic to ologotrophic (Berglund *et al.*, 2001)

A1.3. PBDEs

Wit (2002) reported that BDE-47 is the predominant PBDE in environmental samples collected from areas affected by general pollution.

The tetra and penta brominated compounds are perhaps of most concern since they tend to remain available in the environment, whereas the deca-brominated tend to partition into soils and sediments (Martin *et al.*, 2004).

The acute toxicity of PBDEs are low (Eljarrat *et al.*, 2005).

A1.3.1 Water

Individual PBDEs Concentrations

Table 26 - PBDEs concentrations for the Netherlands water (pg/L) (Hites, 2004).

BDE	47	99	153	209
Netherlands	1.00	0.5	0.1	0.40

Table 27 - Maximum PBDEs concentrations (µg/L) for several world areas (Palm *et al.*, 2002).

	Mono BDE	Di BDE	Hexa BDE	BDE 209
USA, industrial rivers	202700			
Japan		0.01	<0.04	<2.5

A1.3.2 Sediment

Zegers *et al.* 2003, reported that from sediment cores in Western Europe, BDE-47, 99 and specially 209 were present as major compounds. BDE- 28, 100, 153 and 154, were regularly found at lower concentrations. While BDE-75 and 85 were detected occasionally. And BDE-71, 77, 138, 183 and BDE-190 were never detected.

BDE 209 was the major PBDE detected, followed by, 47, 99 and 100, in Spanish coastal sediments (Eljarrat *et al.*, 2005).

And Zhu and Hites (2005) found BDE-153, a major contaminant in lakes.

Song *et al.,* 2004, found that in Lake superior (USA) sediments the most common PBDEs found were: 47,85,128,60,99,100,153,154,183 and 209.

Penta-BDE and tetra-BDE, are the most biologically and environmentally active, and consequently the most hazardous PBDE congeners (Martin *et al.,* 2004).

Individual PBDEs Concentrations

Table 28 - PBDEs concentration in the Cinca River sediment (a tributary of the Ebro river, Spain) (Eljarrat *et al.*, 2005a).

BDE	**ng/g dw**
47	0.2
100	0.1
118	0.3
154	2.9
153	7.8
183	22.8
209	39.9

Table 29 - Environmental concentrations of PBDEs in UK river sediments (Wit, 2002).

BDE	**ng/g dw**
47	368
99	898
71	366
79	1405
83	399

Table 30 - Concentration of flame retardants in sediment from the Scheldt estuary, The Netherlands (Verslyke *et al.,* 2005).

Flame retardants	**ng/g dw**
BDE	
29	0.7
41	4.40
66	0.3
71,75,77	<0.1
85	0.
99	4
100	1.7
119	<0.1
138	0.1

153	1.9
154	1
190	<0.1
209	1650
TBBPA	<0.1
HBCD	71

Table 31 - Concentrations of PBDEs in coastal sediments from Spain (Eljarrat *et al.*, 2005).

BDE	**ng/g dw**
28+33	0.3
47	0.13
66	0.09
77	0.03
100	0.19
99	0.22
118	3.35
154	0.11
153	0.32
183	1.22
209	132.10

Table 32 - Concentration (maximum) of PBDEs in marine sediments from industrialized areas in Japan (Choi *et al.*, 2003).

BDE	**pg/g dw**
47	312.4
28	96.2
99	304.2
100	33.5
154	84.3
153	120
183	660

Table 33 - Concentration of individual BDE (maximum) in surface sediments from Hong Kong Coastal waters (Liu *et al.*, 2005).

BDE	**ng/g dw**
3	7.79
15	1.69
28	5.50
47	1.88
60	0.19
85	0.5
99	8.46
100	0.16
138	1.19

153	5.36
154	2.45
183	14.3
197	11.7
207	11.24
209	2.71

Table 34 - PBDEs river and coastal sediment concentrations, maximum, in Portugal (Lacorte *et al.,* 2003).

BDE	Coastal ng/g dw	River ng/g dw
7	0.05	0.08
11	0.01	
12+13	0.26	0.31
15		0.29
30	0.16	
32		0.13
17		0.16
25		0.04
28+3		0.19
75		1.36
71		17.68
49	0.25	
47	0.45	9.91
100	0.16	0.57
99	0.39	1.64

Table 35 - Surface lake water (Michigan, USA) sediment maximum concentration for several PBDEs congeners (Zhu and Hites, 2005).

BDE	**ng/g**
47	*
99	*
153	0.052
209	315

* Other congeners were detected in low concentrations.

Table 36 - Maximum sediment concentrations (ng/g dw) of several PBDEs around the world (Hites, 2004 and Palm *et al.*, 2002).

Location	Type	Mono BDE	Di BDE	47	99	100	153	154	209
Baltic Sea	Core			0.288	0.176	0.056			2.63
Norway	Core			0.145	0.208	0.070	0.040	0.048	146
UK	Estuary			4.80	6.50				27.9
US	Lake			1.37	3.70	0.63	1.76	1.60	
Korea	Marine			1.14	1.33		0.39	0.41	
Denmark	Marine/fresh			0.16	0.23	0.10	0.04		71.0

Japan		<120	<13	31		28			21
Sweden	Rivers			56.6	14.9	13.7			23.3
UK	Rivers			8.47	14.9				22.0
Netherlands	Rivers			1.10	0.0				
Portugal	Rivers			0.39	0.40	0.24			

Total PBDEs Concentrations

Zhu and Hites (2005) reported, for lakes Michigan and Erie – USA, a total PBDE surface concentration of 320 ng/g dw.

Table 37 - Sediment concentration (maximum) from the Pearl River Delta and China Sea (Mai *et al.,* 2005).

Location	PBDE (total except 209)	209
River	95	7400
Estuary/marine	42	145

Table 38 - PBDE concentrations (ng/g dw) in sediment (maximum) from world rivers and coastal zones (Mai *et al.,* 2005).

Location	ΣPBDEs	BDE-209
Pearl river Delta		
Zhujiang river	49.3	3580
Donjjiang river	94.7	7340
Xijiang river	0.6	77.4
Macao coast	41.3	149
Pear river estuary	21.8	119.9
South China Sea	4.5	9.1
North America		
USA	52.3	
Europe		
UK	1270.8	3190
Netherlands	17.6	510
Sweden	50	7100
Portugal	20	
Spain	34.1	132
Denmark	0.53	21.5
Asia		
Korea	33.8	
Japan	352	11600
China		
Qingdao nearshore	5.5	

Table 39 - Sediment of Lake Superior (USA) (Song *et al.*, 2004).

	ng/g dry mass
ΣPBDE	2
BDE 209	18

Song *et al.,* 2005, reported the total concentration of PBDEs (28,47,66,85,99,100,153, 183,) in Lake Michigan surficial sediments of 1.7 to 4 ng/d dw and 1 to 1.9 ng/g dw in Lake Huron. BDE 209 was present in higher concentrations (100 ng/g dw Lake Michigan and 35 ng/g dw in lake Huron). The higher concentrations of PBDEs were found at the surface.