

**Chapter 4 Atmospheric transport and fate of POP in
remote mountain areas**

Chapter 4. Atmospheric transport and fate of POP in remote mountain areas

The atmosphere is the most important pathway for POP transport to the remote sites (Ballschmiter, 1992; Duce et al., 1991). These compounds have vapour pressures between 10^{-2} and 10^{-5} Pa (see Chapter 2, Table 3) which are in the range of phase changes at the ambient temperature intervals. In this way POP tend to evaporate at ambient temperature rising and condense at temperatures decline. This process has been given many names depending on the phenomenon that was to be explained. “Global Distillation” (Goldberg, 1975), explains processes mimicking a gas chromatograph. Compounds that evaporate faster (less energy needed to change stationary phase for gas phase) will have larger atmospheric mobility than those needing higher temperatures to evaporate and to maintain in the gas phase (4.1). Others have described these processes under names “Global” or “Latitudinal Fractionation”, and “Cold Condensation” or “Selective Trapping” (Wania and Mackay, 1993, 1996; Argell et al., 1999; Grimalt et al., 2001). The principle is the same as the distillation process and has been used to explain the change in POP composition in different environmental matrices in relation to latitude (Calamari et al., 1991; Argell et al., 1999; Ockenden et al., 1998; Kalantzi et al., 2001) and altitude (Calamari et al., 1991; Galassi et al., 1997; Blais et al., 1998; Grimalt et al., 2001). “Grasshopping” is used for the process of POP migration in short jumps, depending on the seasonal changes in temperature at mid-latitudes (Figure 16).

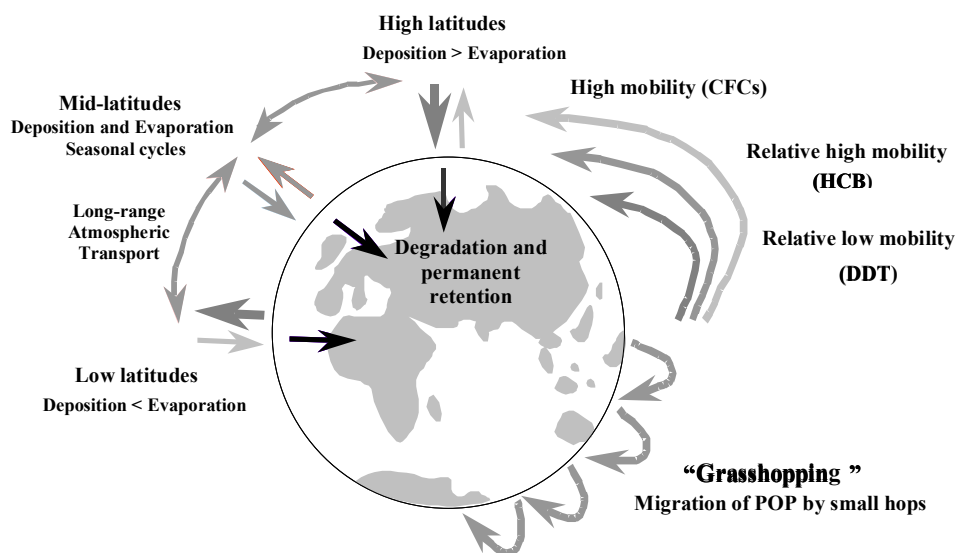


Figure 16. POP migration. Global deposition processes are more significant than evaporation at high latitudes / altitudes and low temperatures (adapted from Wania and Mackay, (1996).

Atmospheric POP appear both in gas and particulate phase. The distribution between the two phases is also temperature dependent (Pankow and Bidleman, 1992). Photo-degradation and deposition are also relevant for the long-range transport of POP (4.2). Once the compounds have deposited on land or superficial water they could be incorporated in these compartments. The retention capacity of soils and lake sediments depend on several factors, such as its organic content, ambient temperatures, biological activity, physical disturbance, chemical transformation, etc. (4.3) (Sanders et al., 1995; Fernández et al., 1999; 2000; Ribes et al., 2002; 2003); Meijer et al., 2003).

4.1 Atmospheric dynamics of POP

The energy needed for POP evaporation/condensation is different for each compound. Table 5 shows the theoretical enthalpies of vaporisation (and condensation) of several organochlorine compounds. The relationship between the vapour pressure and the phase change enthalpies is based on the Gas Law

$$\ln P = - \Delta H_{\text{vap}} / RT + \text{constant} \quad (\text{Hoff et al., 1998})$$

where $\ln P$ is the natural logarithm of the partial vapour pressure (atm or Pa), R is the universal gas constant ($8,3145 \text{ J mol}^{-1} \text{ K}^{-1}$) and T the environmental temperature (K)

Table 5. Theoretical phase change enthalpies of vaporisation from a sub-cooled liquid (Hinkley et al., 1990) for OC pesticides, (Kömp and McLachlan, 1997b) for PCBs)

	ΔH_{vap} (kJ/mol)
α -HCH	68
γ -HCH	70
Endosulphanes	95
4,4'-DDE	87
PCB18	75
PCB28	78
PCB52	81
PCB101	85
PCB110	87
PCB149	90
PCB118	91
PCB153	92
PCB138	97
PCB180	97

Vapour pressure can be transformed into gas phase concentration by adequate change of units.

$$\ln [\text{conc POP}] = - \Delta H_{\text{vap}^*} / RT + \text{constant}$$

where ΔH_{vap}^* is the pseudo-enthalpy. In laboratory studies the plots are calculated for systems in equilibrium. True equilibrium between the atmospheric gas phase and a surface in the environment may not always be the case. The slope of the plot resulting from representation of the previous equation should therefore be considered as the pseudo-enthalpy of phase change. Comparing the slopes of environmental and laboratory data may provide information on the processes of vapourisation or condensation of POP in the environment. The steepness of the slopes may be related to the influence of potential sources on the atmospheric samples (Wania et al. 1998). Steep slopes (high temperature dependence, high pseudo-enthalpies) indicate high surface concentrations in the vicinity of the sampling site. Shallow slopes (low temperature dependence, small pseudo-enthalpies) indicate long-range transport.

4.2 Atmospheric removal pathways

Photo-degradation (4.2.1) and deposition (4.2.2) can eliminate and remove POP from the atmosphere. The former process is irreversible and the latter may be reversible. These processes are important to estimate the atmospheric POP lifetimes. Taking in consideration all these mechanisms, the capacity of POP to stay in the atmosphere can be estimated.

4.2.1 Photo-degradation

One of the possible removal pathways for atmospheric POP is degradation due to direct or/and indirect solar radiation. In the past, few investigations have been done to study the possible effects on POP. Direct degradation, or primary photo-degradation, indicates photo-reactions light with a chemical, either by absorption or by energy transfer from an excited photo-sensitiser. In the second case, indirect degradation, or secondary photo-degradation, refers to photo-reactions of chemicals with photolytically-generated radicals, for example hydroxyl radicals, ozone, singlet oxygen, or a photo-chemically-generated base, which catalyses hydrolysis (Lemaire et al., 1982). So far, no investigation has been performed to study the effect of primary and secondary photo-degradation of POP *in situ*. And only few papers describe experiments under laboratory conditions (Bunce, 1982; Atkinson and Aschmann, 1985; Bunce et al., 1989; Anderson and Hites, 1996a, b; Brubaker and Hites, 1998a, b).

Bunce *et al.* (1982) describes primary and secondary photo-degradation of PCBs in liquids and solids as test media and/or light sources with wavelengths less than 295nm and under high temperatures. These conditions are not found in the environment. However, laboratory experiments using a wavelength 250nm show that the ortho-substituted chloro atoms in the biphenyl molecule have the highest excited-state energies. Furthermore, this study shows that PCBs can be photo-oxidated by direct solar light, even at wavelengths < 300nm (in liquid system). Later Bunce *et al.* (1989) calculated lifetimes for 2-, and 4-chlorobiphenyls (one chlorine substitution) of

less than one week, in an experimental model at wavelengths from 295 – 345nm For 3-chlorobiphenyls (one chlorine substitution) lifetimes of more than one week were calculated. Atkinson *et al.* (1985) and Atkinson (1987) calculated lifetimes of ≈ 8 , ≈ 4 , and ≈ 6 days for respectively 2-, 3-, and 4-chlorobiphenyl after direct photolysis. For higher chlorinated biphenyls the average lifetimes range from a few weeks for dichlorobiphenyls (2 Cl substitutions = 2CB) up to a few months for pentachlorobiphenyls (5 Cl substitutions = 5CB)

OH radical attack is probably the most important photo-degradation pathway for POP in the atmospheric gas phase. This process can modify the levels and the composition of POP in air masses during long-range atmospheric transport. It is however very difficult to measure this process since both POP and OH concentrations should be analysed *in situ* following an atmospheric transact. This air mass should not have any interaction with surfaces or other air masses. Furthermore, both POP and OH levels are very low and OH-radicals have extremely short atmospheric lifetimes (10^{-3} seconds), which is complicating even more their analysis.

Anderson and Hites (1996a, b) described a method of PCB degradation by OH-radicals. OH radicals were generated by the reaction of O_3 and UV light ($\lambda < 320\text{nm}$) and water vapour inside a crystal chamber that was connected to a MS. Injection of cyclohexane and 4,4'-dichlorobiphenyl (2CB) and higher chlorinated biphenyls, up to penta-CB (5 Cl substitutes = 5CB), into this chamber allowed to calculate the degradation of PCB by OH using toluene to calibrate the system. In order to obtain PCBs in the vapour phase, the experiments were done at a temperature range between 323K and 363K ($50^\circ\text{C} - 90^\circ\text{C}$). The temperature dependence of the reaction rates was studied within this interval.

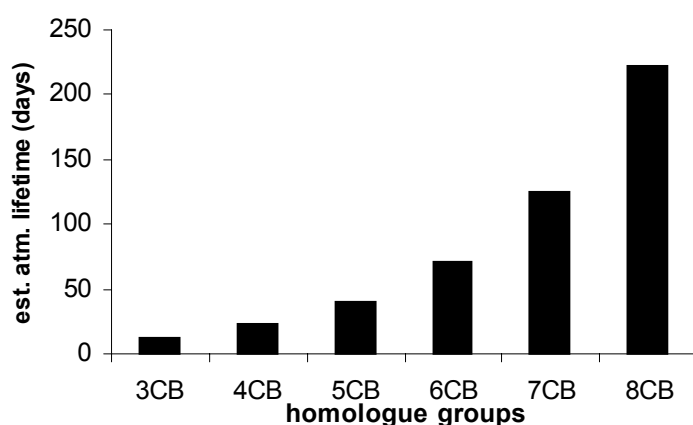


Figure 17. Estimated atmospheric lifetimes of PCB homologue groups due to reaction with OH. Lifetimes calculated based on 24-h global average OH concentration of $8.8 \times 10^5 \text{ cm}^{-3}$ and k_{OH} at 0°C (0-4km altitude) (adapted from Anderson and Hites, (1996b) and Spivakovsky et al., (2000)).

Unfortunately, the temperature interval was not representative of ambient temperatures (213K and 313K = -60°C and 40°C). The same problem occurred with the concentrations of OH radicals and PCBs in the reaction chamber. OH radical concentrations were around 10^9 molecules cm^{-3} , while average ambient concentrations are around 10^6 molecules cm^{-3} (Spivakovsky et al., 2000). PCB concentrations in the experiments were around 10^{14} molecules cm^{-3} , while ambient concentrations are around 10^4 molecules cm^{-3} . In the case of OH radicals there is a difference of 3 orders of magnitude, while in the case of PCBs the differences are about 10 orders of magnitude. Although reaction rates are *a priori* concentration independent, the very high OH and PCB concentrations may cause a situation where there is never a shortage of compounds to undergo the reaction, and thus result in high reaction rates. In contrast, the much lower tropospheric concentrations of the compounds may result in a shortage of one of the compounds for reaction and a reduction of the PCB-OH reaction rates.

The observed temperature dependence was used to extrapolate the reaction rates and atmospheric lifetimes under environmental conditions (first 4km of the troposphere (273K)) for 4,4'-dichlorobiphenyl and higher chlorinated PCBs (Figure 17). For PCBs it seems that higher chlorination slows down the reaction rate, thus increases the atmospheric lifetime. For tri-, tetra- and pentachlorobiphenyls (3CB, 4CB and 5CB) atmospheric lifetimes of 13, 23 and 40 days were estimated, respectively. Anderson and Hites (1996b) only calculated atmospheric lifetimes until pentachlorobiphenyls (PCB#95, #110 and #116). The atmospheric lifetimes for higher chlorinated PCBs can be estimated by extrapolation of the reaction rates of the different homologue groups. These extrapolations give rise to atmospheric lifetimes for hexa-CB, hepta-CB and octa-CB (6CB, 7CB and 8CB) of 71, 125 and 222 days. Although the results obtained are in agreement with the structure-activity tests of Atkinson *et al.*(1985) and Atkinson (1987) one should be cautious upon application of the reaction rates for quantitative calculation of environmental data. However, they may give a good qualitative indication of the atmospheric transformation of PCB. Similar experiments, as done by Anderson and Hites (1996b), were performed by Brubaker and Hites (1998a, b) for HCHs, HCB and PAHs. Atmospheric lifetimes of 120, 96 and 940 days for α -HCH, γ -HCH and HCB, respectively, and 22, 11, 1.5, 26 days for fluorene, phenanthrene, anthracene, and pyrene, respectively, were observed.

4.2.2 Deposition

POP deposition takes place by: 1) snow and rain scavenging of gasses and aerosols (wet deposition), 2) dry particulate deposition and 3) gas exchange with surfaces (Cotham and Bidleman, 1991). POP can occur both in gaseous and particulate phase (aerosols), which depends on the affinity of each compound for a certain particle as well as atmospheric temperature, particle amounts, and particle composition (Pankow, 1987; Pankow and Bidleman, 1992).

4.2.2.1 Wet deposition

Wet deposition involves the transfer of gasses and aerosols to ground surfaces by rain, snowfall, etc. Water solubility and vapour pressure of POP are very important in these processes. If a compound is more water-soluble it will be washed out faster from the atmosphere. The ratio between vapour pressure to the water solubility defines the Henry's Law Constant (H). H-values are used in the calculations for the wash out of gaseous compounds (W_g), and thus the efficiency in which rain (C_{rain}) or snow removes a gaseous compound from the atmosphere ($C_{air\ gas}$) (Cotham and Bidleman, 1991):

$$W_g = C_{rain} / C_{air\ gas} = RT / H \quad (\text{mass/volume})$$

This equation shows that compounds with low H tend to be washed out faster than compounds with high H.

The wash out factor for the particulate phase (W_p) is important for rain and snow scavenging of particle-bounded POP ($C_{air\ particulate}$) (Cotham and Bidleman, 1991).

$$W_p = C_{rain} / C_{air\ part} \quad (\text{mass/volume})$$

However, W_p is very variable and depends, for example, on the size of the particle, its structure and chemical composition, and meteorological conditions.

4.2.2.2 Dry deposition

The dry deposition velocity of particles and particulate-bounded compounds depends largely on the size and composition of the aerosol. For large particles ($>25\mu\text{m}$) gravity is mainly governing the deposition and aerosols are deposited near the emission source. Smaller aerosols, particle sizes between 0.1 and $10\mu\text{m}$, are able to make long atmospheric journeys over more than hundreds of kilometres. Invasions of Saharan dust to the North Atlantic and Europe mainly consist of aerosols of these sizes. Particles smaller than $0.1\mu\text{m}$ depend on molecular diffusion (Cotham and Bidleman, 1991). POP have higher affinity to particles with high than low organic carbon content, due to their relative high lipophilicity ($\log K_{ow} > 4$).

Particulate flux to a surface ($F_{d\ part}$) and the particle-bounded atmospheric concentration of a compound ($C_{air\ part}$) at a given height are related through the dry deposition velocity ($V_{d\ part}$).

$$V_{d\ part} = F_{d\ part} / C_{air\ part} \quad (\text{mass/area}\cdot\text{time})$$

This velocity is very variable and depends on the meteorological conditions, particle size, composition and surface properties.

The adsorption onto soot-carbon (SC) has been shown to affect significantly the overall PAH sorption to certain aerosols (Gustafsson et al., 2001; Bucheli and Gustafsson, 2000; Dachs and Einsenreich, 2000) and is held to be the principal factor of transport of atmospheric particle-bounded PAH to European high-mountain areas (Fernández et al., 2002).

Analysis of wet (rain and snow) and dry deposition annual fluxes in European high-mountain areas have shown that the lighter and lower molecular weights compounds are in general more abundant than the heavier compounds. These lighter compounds occur predominantly in the atmospheric gas phase, while the heavier compounds are essentially particle-bounded (Pankow and Bidleman, 1992). The transfer mechanism of gas phase POP to rain and/or snowflakes is very effective (Carrera et al., 2001; 2002). Thus, wet deposition is accounted to be the predominant pathway of gas phase and particulate phase POP to these mountain areas. The overall transport depends on the quantity of precipitation, which shows high variability between different sites and seasons (Carrera et al., 2001; 2002; Fernández et al., 2003). Although higher PAH levels are observed in the colder season (winter), due to increasing combustion of fossil fuels and reduced photooxidation rates, warmer periods (spring and summer) show highest atmospheric PAH deposition, probably due to high precipitation in these seasons as compares with winter (Fernández et al., 2003). Higher OC deposition is also related to the wet seasons (Carrera et al., 2002).

4.2.2.3 Gas exchange

The exchange of chemical compounds between the gas phase and ground surfaces (soil, water, vegetation) is controlled by the tendency of the compound to be absorbed/adsorbed by these surfaces. The ratio of vapour pressure to water solubility can be used as indicator between levels in the atmosphere and water surface. The ratio between POP levels in octanol and water is used as estimate for the distribution of POP in organic material, giving the octanol-water partitioning coefficient (K_{ow}) (Mackay et al., 1992). Consequently, from H/RT (C_{air}/C_{water}) and K_{ow} ($C_{octanol}/C_{water}$) one can obtain the octanol-air partitioning coefficient (K_{oa}),

$$K_{oa} = K_{ow} RT / H$$

which can be used as the indicator for the distribution of POP between the atmosphere and (organic) surface (Kömp and McLachlan, 1997a). Since H is temperature dependent, K_{oa} is temperature dependent as well (Kömp and McLachlan, 1997b). Thus, there can be a flux from the air to the surface (surface is sink), or from the surface to the atmosphere (surface is source). This exchange is complex and depends on many factors, like, properties of compound, meteorological conditions, especially temperature, surface area, and thickness of boundary layers between environmental compartments.

Vegetation has been used in the past as indicator for atmospheric contamination on small and global scale (Calamari et al., 1991; Simonich and Hites, 1995; Kömp and McLachlan, 1997a).

Although there are important differences between species, in general the lipophilic organic pollutants ($\log K_{ow} > 4$) are exclusively taken up from the atmosphere via the cuticle waxes or by the stomata of the leaf, where they tend to accumulate in the leaf. Uptake of these compounds from the soil via the roots is not significant, neither are POP transported to other parts of the plant. Due to the large surface area of leaves, atmospheric variability of POP levels and ambient temperatures affect directly the concentrations found in the leaves of plant species (Simonich et al., 1995). In remote sites leaves can therefore be useful as bio-indicators POP levels, since they are easily collected and most POP have $\log K_{ow} > 4$.

4.2.3 Atmospheric persistence and long-range transport

As mentioned before, the atmospheric behaviour of POP is mainly controlled by the physical conditions of the atmosphere and the physico-chemical properties of the compounds. Atmospheric lifetime is used to study the air persistence of the compounds and their feasibility to undergo long-range transport. Gramatica *et al.* (2001) modelled the atmospheric half-lives of 12 POP and 48 additional compounds that could be POP, using different molecule structure descriptors in a regression QSAR (Quantitative Structure-Activity Relationships) model. In these QSAR models the environmental chemical properties were calculated by combination of the molecular structures and physico-chemical properties of the compound with environmental conditions using several statistical tests (PCAs). Indices for atmospheric persistence and long-range transport were obtained (Table 6). These indices may be useful for a first evaluation of the atmospheric mobility of POP. Other models are based on fugacity calculations (Mackay et al., 1992; Beyer et al., 2000).

Table 6. Atmospheric half lives of some POP (adapted from Gramatica *et al.*, (2001))

Name	Atmospheric half life values (h)	
	Average	maximum
Fluorene	37,2	67,6
Anthracene	1,1	1,7
Phenanthrene	11,0	20,0
Fluoranthene	11,2	20,4
Pyrene	1,3	2,0
Chrysene	4,4	7,9
Benz[a]anthracene	2,0	3,0
Benzo[b]fluoranthene	7,9	14,5
Benzo[a]pyrene	0,7	1,1
Benzo[ghi]perylene	1,8	3,2
Dibenz[ah]anthracene	2,3	4,3
PCB18	525	724
PCB28	586	724
PCB52	1023	1445
PCB101	2138	2884
α -HCH	51	93
γ -HCH	51	93
HCB	20417	37154
4,4'-DDT	98	178
4,4'-DDE	98	178

The atmospheric half-lives PAH may be hours or days. Those of organochlorine pesticides, α -HCH, γ -HCH, 4,4'-DDE and 4,4'-DDT, of days or weeks, and PCBs of weeks or months. HCB has the largest atmospheric half-life encompassing a few years (Table 6).

The atmospheric half-lives of PCBs are somewhat higher than the residence times estimated from OH radical reactions of Anderson and Hites (1996b). Recently the atmospheric degradation of PCBs by OH radicals has been evaluated (Axelman and Gustafsson, 2002). Application of the reaction rates as observed by Anderson and Hites (1996b) on environmental data would result in one order of magnitude faster depletion of the less chlorinated PCBs (more reactive) in comparison to the more chlorinated PCBs (less reactive). However, there are no temporal and spatial trends observed in environmental samples that give evidence for an such enhanced depletion of less chlorinated PCBs. For example, the composition of PCB congeners is more or less the same along historical samples, such as sediment cores (Sanders et al., 1995). Moreover, the estimated quantity of degraded PCBs is of such an amount that it would outnumber the loss of PCBs from the environment by other processes, such as sink to oceanic sediments. Even in a scenario of maximum annual PCB emissions (Breivik et al., 2002) this would not be enough, by orders of magnitude, to compensate for the annual loss of PCBs by OH radical reactions. As mentioned before, the experimental conditions under which the PCB-OH reaction rate constants were obtained may be too far from the environmental conditions. Application of these rate constants may lead to an overestimation of the atmospheric loss of PCBs, especially on the more volatile and reactive congeners.

The work of Junge (1974) can be used as an alternative to estimate the atmospheric residence times of chemical compounds. Studying a large set of field data from different trace gasses provides an empirical relationship between the tropospheric residence time (τ_{total} (year)) and the tropospheric variability in concentrations. This relation is described as:

$$\tau_{\text{total}} = 0.14 / \text{RSD}_{\text{total}}$$

where $\text{RSD}_{\text{total}}$ is the total variability observed in the concentrations expressed as a relative standard deviation (standard deviation divided by mean concentrations). The inverse of the residence time is a compilation of the different processes involved in the loss of compounds from the troposphere, such as degradation and deposition. The tropospheric residence time can therefore be described as:

$$1/\tau_{\text{total}} = 1/\tau_{\text{react}} + 1/\tau_{\text{dry dep}} + 1/\tau_{\text{wet dep}}$$

where τ_{react} is the residence time due to chemical reactions, $\tau_{\text{dry dep}}$ is the residence time due to dry deposition and $\tau_{\text{wet dep}}$ is the residence time due to wet deposition. Each of these processes also includes several other processes. However, τ_{react} is here assumed to be τ_{OH} ; the residence time due

to reactions with OH radicals. If τ_{OH} is longer than τ_{total} there should be other loss processes more important than the reaction with OH radicals. If τ_{OH} is shorter than τ_{total} then one of the estimates is wrong (Axelman and Gustafsson, 2002).

Values for τ_{total} were calculated from year round atmospheric samples collected at remote sites on the Northern and Southern Hemisphere (see Results. Global-Soc database). For the less chlorinated CBs (3CB, 4CB and 5CB) τ_{OH} is shorter than τ_{total} , while τ_{OH} for the more chlorinated CBs (6CB and 7CB, and probably 8CB) is longer than τ_{total} (Figure 18). This indicates that for the more chlorinated PCB other loss processes, like deposition, are more important than OH radical reaction. The fact that the less chlorinated PCB show slightly higher τ_{total} than the more chlorinated PCB shows that the tropospheric variability is not under influence of OH radical reaction, since these reactions would evidence shorter residence times for these compounds. Alternatively, residence times calculated by the Junge equation could be over-estimated.

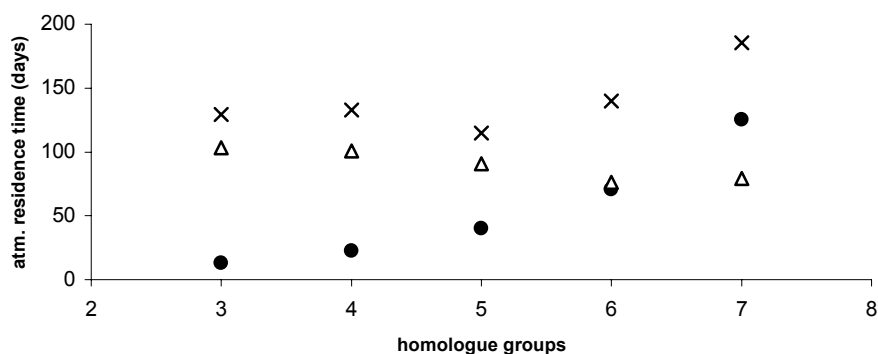


Figure 18. Residence times (in days) of τ_{OH} (black dots), τ_{total} (triangles) and τ_{real} (stars) for the different homologue groups of PCBs.

The atmospheric samples are collected with HiVol samplers and analysed in laboratories. During sample handling and analytical procedures several steps could add an error to the observed variability. This variability could be called 'sample+analysis' variability. Although, no value exists for the collected samples an attempt was made to obtain the ' $\tau_{sample+analysis}$ '. In this case, one sample was injected four times during one year and analysed on PCB congeners. The obtained relative standard deviation range from 0.1 to 0.3 for the different PCB congeners, which is consistent with the 0.1 from Oehme et al. (1996). The real residence time (τ_{real}) is expressed as:

$$\tau_{real} = 1/\tau_{total} - 1/'\tau_{sample+analysis}' \quad (\text{Axelman and Gustafsson, 2002})$$

Applying this 'correction' to the total residence time, figure 18 shows that τ_{OH} is even further separated from the residence times based on the Junge model. Now, less chlorinated PCBs (3CB,

4CB and 5CB) have similar or slightly lower residence times than the more chlorinated PCB (6CB and 7CB, and probably 8CB). These results might indicate that the OH reactions have influence on the less chlorinated PCBs but that the reaction rates are not the ones calculated by Anderson and Hites (1996b). Application of the Junge model to estimate the tropospheric residence time of PCBs does not allow to elucidate which fraction is removed irreversibly from the troposphere (photodegradation) and which fraction is removed reversibly (deposition). Deposited PCB could re-volatilise and form part again of the troposphere. Application of the Anderson and Hites (1996b) reaction rates may indicate which is the loss of PCBs from the troposphere, however, the very high PCB loss is not realistic in comparison to other loss process and emission data. Moreover, there are no evidences in environmental data that such a depletion takes place. One way or another, the findings suggest that there is still a wide gap of knowledge in the understanding of the atmospheric fate of these compounds.

4.3 Retention of POP in soils and sediments

On a global scale only a small percentage of soils and sediments receive POP from direct input. In the case of most POP these soils are situated on the Northern Hemisphere between 30° - 60°N. Remote background soils, for example, occupy more than 99% of the total soil surface. These are soils where POP are deposited after long-range atmospheric transport and where atmosphere and soil surface are in certain state of equilibrium (Meijer et al., 2003). When POP are deposited on water surfaces sedimentation processes can take place and particle-bounded POP can be incorporated into sediments. Although many factors influence soil and sediment retention capacity for POP, in general, both compartments act as significant sinks for these compounds in remote areas (Fernández et al. 1999; 2000; Ribes et al., 2002; Meijer et al., 2003). In the past few years, accumulation of POP in soils and sediments have been used to reconstruct the historical input of these compounds to source and remote areas (Sanders et al., 1994; Fernández et al., 2000).

4.3.1 POP in remote soils

Soils can be used as spatial and temporal indicators for the atmospheric levels and deposition levels of POP (Sanders et al., 1995; Meijer et al., 2003). As mentioned before (4.2.2.3) the exchange between the atmosphere and surface, which could be soil, is depending on the concentrations in the both compartments as well as the properties of the compound, the soil and the atmosphere. Factors which *a priori* favour the POP transfer from atmosphere to soil, or the POP retention in soil, are relatively high air POP concentrations, low ambient temperatures, low soil POP concentrations and high soil organic carbon content (Fernández et al, 2000; Ribes et al, 2002; Meijer et al, 2003). Low ambient temperatures and high organic carbon content have also influence on the POP sorption in soils. Soil samples collected on the Island on Tenerife at 26 altitudes between 10m and 3400m have shown a very good positive correlation between OC levels

and the organic matter in the soils. Moreover, the concentration of most of the analysed OC increased with altitude, so when temperatures decrease (Ribes et al, 2002). The partitioning of POP between soil and air can be expressed as

$$K_p = C_{\text{soil}} / C_{\text{air}} \quad (\text{volume} / \text{mass})$$

where K_p is the soil-air partitioning coefficient and C_{soil} the POP concentration in soil (mass / mass) and C_{air} the POP concentrations in the atmospheric gas phase (mass / volume).

Prediction of POP partitioning between the soil and atmosphere can be done using the octanol-air partitioning coefficient (K_{oa}). As mentioned in 4.2.2.3. this coefficient is temperature dependent. Further on, the soil organic content and the properties of the organic matter have also to be considered (Finizio et al, 1997; Harner et al, 2001). The partitioning of POP between soil and atmosphere can be expressed as

$$K_p = f_{OM} (\xi_{OCT} / \xi_{OM})(MW_{OCT}/MW_{OM} \delta_{OCT}) K_{oa}$$

where f_{OM} is the fraction of organic matter in soil, and ξ_{OCT} and ξ_{OM} are the activity coefficients of the individual POP in octanol and organic matter, respectively. MW_{OCT} and MW_{OM} are the molecular weights of octanol and organic matter, respectively, and δ_{OCT} is the octanol density (0.820 kg L⁻¹; at 20°C). After the assumptions that

$$f_{OM} = 1.5 f_{TOC}$$

$$(\xi_{OCT} / \xi_{OM})(MW_{OCT}/MW_{OM}) = 1$$

where f_{TOC} is the fraction of total organic carbon in the soil, the K_p is given by

$$K_p = 1.5 (f_{TOC}/\delta_{OCT}) K_{oa}$$

This adsorption model requires only knowledge on two easily measurable parameters, K_{oa} and f_{TOC} .

However, besides temperature and organic matter, POP retention in soils could additionally influenced by processes, such as biodegradation, formation of non-extractable residues, and transfer to depths. The last process can both take place by bioturbation as well as by infiltration of precipitation (Meijer et al, 2003). In soils of the high-mountain areas biological activity is slow, due to low temperatures, thus it can be assumed that biodegradation and bioturbation will be of small influence for POP retention in these soils.

4.3.2 POP in remote lake water and sediments

Lake sediments of remote high-mountain areas can be considered as archives of lake response to anthropogenic pollution and climate changes (Guilizonni et al, 1998; Kamenik et al, 2000; Fernández et al, 2000). They include mineral particles and dissolved ions from run-off from the lake catchment and atmospheric deposition. Further more, there is a fraction of biogenic inorganic material, including diatoms frustules, remains of zooplankton and benthic organisms, and calcium carbonates (Guilizonni et al, 1998). The organic fraction consists of resistant substances of vegetal and animal origin, like pigments, pollen, etc., but they can also contain significant amounts of POP from atmospheric deposition.

The input of POP to the lake is directly related to atmospheric deposition. Depending on the physico-chemical properties of the compound and the physical conditions of the atmosphere, the compounds may enter the lake dissolved in rain drops, absorbed or adsorbed in/to particles and snow flakes, and dissolved or particle-bounded in the run-off from the lake catchment after rainfall or snowmelt (see 4.3.3). Once POP have entered the lake new interactions may take place between the compounds and particles in the lake waters. This depends on their water solubility, or their affinity to organic material, as well as on the physical conditions, like the temperature, in the water column (Karickhoff et al, 1979; Chiou et al, 1983; Mackay and Powers, 1987; Baker et al., 1991; Swackhamer and Skoglund, 1993). The POP with relatively high solubility, like the HCHs, are present in the dissolved phase, while PCB and PAH are in general more related to the particles in the water column (Vilanova et al., 2001a, b, c). Although atmospheric POP levels in different European high-mountain lakes are lower than in lakes at lower altitude, relatively high concentrations of γ -HCH and endosulphanes are detected in Estany Redon (Central Pyrenees) in springtime (Vilanova et al., 2001c). Their occurrence is related to the application of these products for agricultural purposes in the European continent. Other OC show a relative constant distribution round the year. Uniform POP distributions are observed in the water column once they have entered to lake waters. Part of the dissolved POP may be absorbed actively or passively by zooplankton and phytoplankton species, or by higher organisms, such as fish, via ingestion, respiration, and diffuse absorption (Vives et al. 2004). Further on, fish have the ability to ingest particles and zoo/phytoplankton species from the water column or sediments (Varanasi, 1989; Baumard et al., 1998). Inside organisms some compounds will accumulate in body tissue, while others will be transformed to other compounds by metabolism or excreted in its original form (Barron, 1990; Clark et al., 1990; Gobas et al., 1993; Spacie et al., 1995).

The degree of contamination of the aquatic system can be assessed by comparing the concentrations of pollutants in young sediments (top layer) with values in older (deeper) sediments. The average level in the later can be used as baseline value for the lake system. Analysis of a certain section of the sediment could evaluate not only the degree of contamination but also the temporal trend. In this case the chronology of the core is necessary. This is normally estimated from the

changes in concentrations of natural radioactivity. The natural fallout of lead-210 (^{210}Pb) can be used for these purposes. ^{210}Pb is produced at a steady rate by decay of radon gas (^{222}Rn) in the atmosphere. Attached to particles ^{210}Pb is deposited on the lake surface and further transported through the water column to form part of the sediment. The buried ^{210}Pb undergoes radioactive decay with a half-life of 22.3 years. When sediments are collected and the ^{210}Pb concentration is measured, it is possible to calculate the time span at which each layer was buried. ^{137}Cs and ^{241}Am can also be used for dating as complementary tools. They are consequence of the weapon fallout and nuclear power accidents, such as Chernobyl (1986) (Appleby and Oldfield, 1978; Appleby, 2001).

4.4 Environmental fate of POP in remote high altitude areas

Figure 19 shows a graphical summary of the transport and fate of POP to high-mountain areas in general and specifically lakes, based on the information presented in the former paragraphs. Due to the lack of local sources POP enter the high-mountain ecosystems after long-range atmospheric transport. During this transport some degree of photo-oxidation could take place for certain compounds, which influences the levels and composition of the POP. Once they are deposited they can become part of the soils, lake waters, organisms and eventually lake sediments. The principal factors responsible for the presence of POP in these areas are semi-volatility, resistance against degradation, and the ambient temperatures.

One can conclude that the remote high altitude areas constitute an ideal system for the analysis of long-range atmospherically transported POP, because

- 1) atmospheric transport is the only input,
- 2) long residence times of POP in these oligotrophic systems,
- 3) retention of certain POP because of low temperatures,
- 4) slow sedimentation rate in these lakes because of low primary production,
- 5) low biodegradation in soils, lake waters and sediment because of low temperatures,

These characteristics have favoured the concentration of POP in thin soil or sediment layers. Further more, the low ambient temperatures enhance their accumulation. This results in concentration rather than dilution effects of certain POP after long-range atmospheric transport to these areas (Blais et al., 1998; Fernández et al., 2000; Grimalt et al., 2001). More over, since lower ambient temperatures are related to higher altitudes increases are observed for the concentration of certain organochlorine compounds with increasing altitude (Blais et al., 1998; Grimalt et al., 2001).

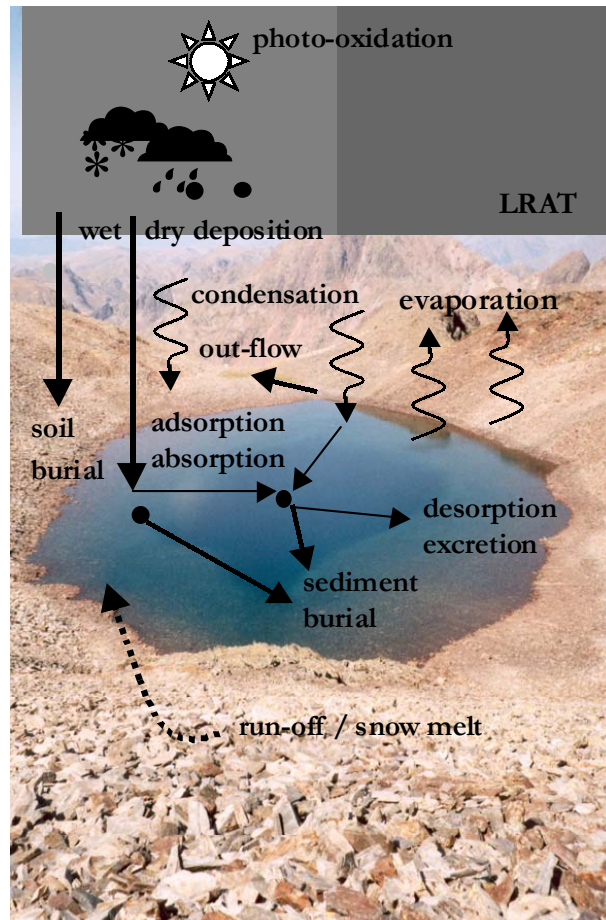


Figure 19. Atmospheric transport and fate of POP in remote high-altitude mountainous areas

Chapter 5 Methods and Materials

Chapter 5. Methods and Materials

5.1 Atmosphere

Between June 1999 and January 2003 atmospheric samples were collected for POP analysis on the Island of Tenerife (June 1999 – July 2000), the Central Pyrenees (November 2000 – January 2003), and the High Tatras (June 2001 – June 2002). The sampling method was the same for all these sites. In the case of Tenerife and High Tatras the collected samples were sent to the analytical laboratory in Barcelona by aeroplane, while in the case of the Central Pyrenees the samples were transported by car to the same laboratory. The general sampling and analytical method are presented in 5.1.1. Paragraph 5.1.2 and 5.1.3 deal with the back-trajectories and temperature determination, respectively. This additional data is used for the interpretation of atmospheric data in terms of origin of sampled air masses and temperature dependence. Atmospheric deposition samples have been collected on the Island of Tenerife between June 1999 and June 2000. The sampling and analytical methods are presented in 5.1.4. Identification and quantification of the analysed POP in the extracts are presented in 5.1.5.



Figure 20. HiVol-sampler for atmospheric gas and particulate sampling on the border of Estany Redon.

Figure 21. Deposition sampler at the Atmospheric Observatory of Izaña. On the background the peak of Teide is visible (Foto: Sandra Ribes)

5.1.1 Atmospheric gas and particulate phase

Air was collected with a high volume (HiVol-) sampler (MCV S.A., Collbato, Catalonia, Spain) (Figure 20). POP in the gas phase were extracted from the air matrix with two polyurethane foam (PUF) plugs (diameter 6 cm; height 10 cm; density 28.5 kg/m³) packed inside a Teflon[®] tube. Glass fibre filters (GFF; type GF/B; 20.3 x 25.4 cm; 1.6 µm pore size; Whatman International Ltd., Maidstone, England) were used to collect the particulate phase. Before sampling PUFs were Soxhlet extracted with *n*-hexane (Merck, Darmstadt, Germany) for 48 hours. GFFs were cleaned by ashing at 400°C for 24 hours. PUFs were packed into the Teflon[®] tubes which were subsequently wrapped in aluminium foil and introduced to heat sealable polyester bags (Kapak corporation, Minneapolis, USA) and stored at -20°C before transport to sampling sites. GFFs were also wrapped in aluminium foil and introduced into the heat sealable polyester bags and stored at -20°C before transport. Storage had a duration of about 2 days then PUFs and GFFs were transported to sampling sites below 0°C in a coolbox containing dry ice. Transport to Tenerife and High Tatras took approximately 2 days.

At the Island of Tenerife and the High Tatras the HiVol-sampler was energy supplied by the electric circuit of the meteorological stations, while at Estany Redon a power generator was used. This generator was always situated upwind from the HiVol-sampler at a minimum distance of 50m. In the Central Pyrenees and High Tatras the HiVol-sampler was installed at ground level where it sampled air at 1.5m height. At Tenerife the sampler was installed on a 15m high tower, in the case of Izaña, and on a 40m high lighthouse, in the case of Punta de Hidalgo. Collected sample volumes were between 80 m³ and 280 m³. Every sampling period had one field blank for PUFs and GFFs. The field blanks were also introduced but without running the pump. After sampling the PUFs and GFFs were wrapped in aluminium foils and stored in heat sealable polyester bags, placed inside a coolbox and transported below 0°C to the laboratory in Barcelona.

Injection of PCB#30 and PCB#209 *in situ* to the samples and blanks after sampling did not show significant losses during transport (recoveries >81%). After this, the surrogates were added to samples and blank in the laboratory. PCB#30 and PCB#209 were added as internal standards for OC analysis and anthracene-d₁₀ and benzo(ghi)perylene-d₁₀ for PAH analysis. The recoveries of these compounds were used to correct for losses during transport and analysis. Table 7 shows the average recoveries for the gas and particulate phase.

PUFs and GFFs were Soxhlet extracted for 24 hours in 250 mL *n*-hexane and in 250 mL hexane:dichloromethane (DCM) (Merck, Darmstadt, Germany) (4:1 v/v), respectively. The extracts were vacuum evaporated until 1 mL. Samples and blanks were cleaned-up by adsorption on 2 g of aluminium oxide (Fluka Type 507C, Fluxa AG, Switzerland) and elution with 8 mL of hexane:DCM (9:1 v/v) and 7 mL of hexane:DCM (1:2 v/v). The 1st fraction contained most of the OC (HCB, PCBs, DDTs), while the 2nd fraction contained the PAH, HCHs and endosulphanes. The collected fractions were vacuum evaporated to 1 mL and to near dryness under a gentle stream of nitrogen.

Finally, they were re-dissolved in iso-octane (Merck, Darmstadt, Germany) to 50 μL and stored at -20°C before injection in a gas-chromatograph.

5.1.2 Back-trajectories of air masses

The origins of the sampled air masses at Tenerife (Izaña and Punta de Hidalgo), Central Pyrenees (Estany Redon), and High Tatras (Skalnáté Pleso) were calculated from back-trajectories using the HIRLAM model (High Resolution Limited Area Model) of the Spanish National Institute of Meteorology (INM). This model is based on isentropic surfaces that provide a more realistic representation than those elaborated from isobaric surfaces (Danielsen, 1961; Merrill et al., 1986). The calculations were performed at 00:00 UTC and 12:00 UTC for five days (5-D) back with one hour step. The isentropic surfaces for each back-trajectory at the atmospheric sampling sites were selected according to the observed potential temperature at the altitudes of the sites. The calculations of back-trajectories were done by Carlos J. Torres-Garcia (Atmospheric Observatory of Izaña, INM, Tenerife, Spain)

5.1.3 Atmospheric temperatures (T_a)

The T_a for the atmospheric sampling periods on Tenerife were obtained from the records of the Atmospheric Observatory of Izaña of the INM. For the Central Pyrenees T_a were obtained from the records the automatic weather station (AWS) situated at the border of Estany Redon and at the Centre of High Mountain Research (CRAM; 1600m). At Estany Redon, T_a were calculated from measurements taken every 30 min. At CRAM, T_a were calculated from the minimum and maximum daily temperatures. In the High Tatras at Skalnáté Pleso the mean atmospheric temperatures for each sampling period were obtained from the registers of the Slovakian Meteorological Institute (SAV) which has a meteorological station at sampling site.

5.1.4 Atmospheric deposition

From June 1999 until June 2000 deposition samples were collected at Izaña on top of a 15m tower. They were collected in stainless steel reservoirs ($\varnothing = 24$ cm, $A = 452,4$ cm²) using a Model ARS 1010 sampler (MTX, Italy) (Figure 21). Each sampling period encompassed approximately two weeks. After this time the reservoirs were carefully rinsed with Milli-Q water in three successive steps and the rinses were collected together. Blanks were taken before each sampling. Both samples and blanks were filtered with pre-weighted glass microfibre filters (GFF) (Whatman, Maidstone, England (4,7 cm)). These filters were previously cleaned by ashing at 400°C for 24 hours. After filtration the dissolved phase was extracted using Empore extraction C-18 disks (3M Empore, Harbor City, USA). Vacuum was used to increase the speed of filtration/extraction. PCB congeners #30 and #209 were introduced in both GFF and C-18 disks as internal standards before sample introduction. Then, the GFFs and C-18 disks were wrapped in aluminium foil,

placed in polyester bags and stored at -20°C . These bags were introduced in a coolbox for air transport to Barcelona (approximately 2 days) where they were kept at 0°C .

In the laboratory the C-18 disks were successively extracted with methanol, cyclohexane and dichloromethane (5 mL each) (Merck, Darmstadt, Germany). Sample handling is described in detail elsewhere (Carrera *et al.*, 1998). GFFs were Soxhlet extracted for 24 hours in 100 mL of hexane:DCM (4:1 v/v), respectively. This extract was vacuum evaporated to 1 mL. All samples and blanks were cleaned up with 2 g of alumina and 8 mL of hexane:DCM (9:1 v/v) and 7 mL DCM:hexane (2:1 v/v). The collected volume was vacuum evaporated to 1 mL and further concentrated to 50 μL in isooctane (Merck, Darmstadt, Germany) under a gentle stream of nitrogen. Then extracts were stored at -20°C before injection to a gas-chromatograph for quantification.

5.1.5 Quantification of atmospheric samples

5.1.5.1 Identification and quantification of OC

Before instrumental analysis tetrachloronaphthalene was added to the vials for correction of possible instabilities. The extracts were injected into a gas chromatograph equipped with an electron capture detector (GC-ECD, Hewlett Packard 5890 Series II). A 50 m fused silica capillary column (0.25mm i.d, 0.25 μm film thickness) coated with 5% phenyl 95% methylpolysiloxane (DB-5, J&W Scientific, Folsom, CA, USA) was used for the analyses of HCB, PCB congeners (#18, #28, #52, #70, #101+90, #110, #149+123, #118, #153, #105+132, #138, #158+160, #180, #199, #194), DDTs (4,4'-DDE and 4,4'-DDT) and for the first identification and quantification of HCH (α -HCH and γ -HCH). The oven temperature program was started at 100°C (holding time 1 min), increased to 150°C at $15^{\circ}\text{C min}^{-1}$, followed by heating at $4^{\circ}\text{C min}^{-1}$ to 240°C (holding time 12 min) and finally increased to 300°C at $4^{\circ}\text{C min}^{-1}$ (holding time 10 minutes). Injector (split/splitless mode) and detector temperatures were 280°C and 310°C , respectively. Helium and nitrogen were used as carrier (0.33mL min^{-1}) and make-up (60mL min^{-1}) gases, respectively. For the confirmation of the quantified HCHs (α -HCH and γ -HCH) and the analysis of endosulphanes (α -endosulphane and β -endosulphane) the extracts were analysed on a gas chromatograph coupled to a mass spectrometer with negative ion chemical ionisation (GC-MS-NICI). A Fisons MD 800 instrument (quadrupole-detector, THERMO Instruments, Manchester, UK) was used. The instrument was equipped with a capillary column HP5-MS (30m x 0.25mm i.d. x 0.25 μm film thickness). Helium was used as carrier gas (1.1mL min^{-1}). The oven temperatures were programmed from 90°C (1 min) to 120°C at $15^{\circ}\text{C min}^{-1}$ and then to 300°C at $4^{\circ}\text{C min}^{-1}$ with a final holding time of 10 min. Samples were injected in split/splitless mode at 280°C . In the GC-MS-NICI, ion source and transfer line temperatures were 150°C and 280°C , respectively. Ammonia was used as reagent gas. Ion source pressure (currently 1.6 Torr) was adjusted to maximize the perfluorotributylamine ions (m/z 312,

452, 633, and 671). Ion repeller was 1.5 V. Data were acquired in selected ion monitoring mode with dwell time of 0.06 s and span of 0.10 amu. The ions selected for α -HCH and γ -HCH were m/z 71 and 255, respectively. α -Endosulphane and β -endosulphane were selected with m/z 406 and 272, respectively (Chaler et al., 1998).

The external standard method was used for the identification of the peaks in the chromatograms corresponding to the different retention times of the compounds on the column and to quantify the OC. The compounds in this standard were from Dr. Ehrenstorfer (Ausburg, Germany). The concentration range of the external standards covered the range of compound concentrations found in the samples.

Detection limits (determined as three times the standard deviation of the chromatographic noise near the peaks of the analysed compounds) were 0.04-0.23, 0.03, 0.20, 0.08, 0.12-0.15 and 0.05-0.11 pg m^{-3} for PCBs, HCB, 4,4'-DDE, 4,4'-DDT, HCHs and endosulphanes, respectively.

5.1.5.2 Identification and quantification of PAH

The quantitative analyses were carried out by gas chromatography coupled to mass spectrometry. Samples were injected in an Agilent 6890 series chromatograph equipped with a 30m fused capillary column (HP-5MS, 0,25mm x 0.25 μm film thickness). The oven temperature program started with 90°C held for 1 min., then it was heated to 130°C at 12°C min^{-1} and to 310°C at 7°C min^{-1} . The temperature was kept at 310°C for 10 minutes. The injector, ion source, quadrupole and transfer line were 280°C, 200°C, 150°C and 280°C, respectively. Helium was used as carrier gas (0,9 ml s^{-1}). A MS selective detector Agilent 5973 series was operating in selective ion monitoring (SIM) with electron impact (71eV). Dwell time was 50 ms channel⁻¹. PAH were selected on the following ions: fluorene ($m/z=166$), phenanthrene ($m/z=178$), anthracene ($m/z=178$), fluoranthene ($m/z=202$), pyrene ($m/z=202$), benz(a)anthracene ($m/z=228$), chrysene+triperylene ($m/z=228$), benzo(b)fluoranthene ($m/z=252$), benzo(k)fluoranthene ($m/z=252$), benzo(e)pyrene ($m/z=252$), benzo(a)pyrene ($m/z=252$), indeno(1,2,3-cd)pyrene ($m/z=276$), dibenz(ah)anthracene ($m/z=278$), and benzo(ghi)perylene ($m/z=276$). The quantification was performed by external standard method and corrected for surrogate recoveries of anthracene-d₁₀ ($m/z=188$) and benzo(ghi)perylene-d₁₀ ($m/z=288$), added to the samples and blanks before extraction. The recoveries of the surrogates are presented in Table 7. The compounds in this standard were all from Dr. Ehrenstorfer (Ausburg, Germany). Detection limits range between 100 and 400pg for the individual compounds in the samples.

5.2 *Pinus uncinata* and SPMD

Both *Pinus uncinata* and semi-permeable membrane devices (SPMD) can be considered as passive samplers for atmospheric gas phase, since their surfaces are subject to the exchange of gasses, and thus could be used as monitoring systems for atmospheric contamination. The

principles of the exchange process are explained elsewhere (paragraph 4.2.2.3). In the following paragraphs some specific characteristics of the samplers are indicated as well as some aspects of the exchange mechanism of atmospheric OC. Sampling of the leaves of *Pinus uncinata* is presented in 5.2.1 and the SPMD sampling and analytical method is presented in 5.2.2. Identification and quantification methods for the analysis of OC will be presented in paragraph 5.2.3.

Figure 22. *Pinus uncinata* is the uppermost growing tree in the Central Pyrenees. The presented specimen is growing at 2250m near Estany Redon.

5.2.1 *Pinus uncinata*

PCB have high octanol/water partitioning coefficients ($\log K_{ow} > 4$) and show affinity for organic materials such as pine tree needles (Umlauf et al., 1994; Simonich and Hites, 1995). In this respect, the pine species, *Pinus uncinata*, constitutes the dominant tree species at the timberline (1700-2400m) of the Central Pyrenees (Figure 22). This species can therefore be useful as sentinel plant for atmospheric pollution in these remote alpine-subalpine zones. In the present thesis, the potential of *Pinus uncinata* to monitor long-range transported pollution to the high-mountain lake Estany Redon (Central Pyrenees) is investigated. The concentrations in the leaves can be compared with atmospheric PCB data. Based on concentrations of PCBs in the air and leaves one can interpret the state of equilibrium and see if external factors, like temperature, have influence on this equilibrium. Since temperature decreases with increasing altitude the species has been measured in an altitude gradient between 1750 m and 2250m.

5.2.1.1 Sample collection and analytical procedure *Pinus uncinata* leaves

Samples between 1750m and 2250m were collected in March and June 2002 with pre-cleaned tweezers, stored in glass tubes and transported to Barcelona at $< 0^{\circ}\text{C}$. There, they were stored at -20°C until analysis. Whole pine needles (1-4 g fresh weight) of each sample were Soxhlet extracted for 24 h in 100 mL DCM inside a pre-cleaned glassfiber cartridge (Whatman Ltd) containing 5 g Na_2SO_4 (Merck, Darmstadt, Germany). Internal standards of PCB#30 and PCB#209 were added to all samples and blanks before extraction. Then, the extract was evaporated until 0.5 mL by vacuum rotary evaporation and clean up with a two-layer column (diameter 1 cm) filled with slurry packing in hexane with 8 g of silica gel (Panreac, Barcelona, Spain) (bottom) and with 8 g neutral aluminium oxide (top). The column was topped with 0.5 g of Na_2SO_4 . Aluminium oxide, silica gel and sodium sulphate were activated overnight at 400°C , 120°C and 110°C , respectively. Aluminium oxide and silica gel were deactivated with 5% Milli-Q H_2O . The column was then eluted with 20 mL of hexane and additionally with 20 mL hexane: DCM (19:1 v/v) for PCB elution. The recovered fractions were vacuum evaporated to 0.5 mL, transferred to vials and then further concentrated under a gentle N_2 -gas stream and redissolved in 50 μL of isooctane.

5.2.1.2 Dry weight and hexane-extractable lipid content

Dry weight (DW) and hexane-extractable lipids (HEL) were determined from sample aliquots (0.5-2 g). These aliquots were dried at 100°C for 24 hours in a hot air oven for DW. For HEL the dried needles were extracted two times with 20 mL of hexane in a ultrasonic bath for 15 minutes. The combined extracts were then vacuum evaporated to 0.5 mL and transferred to a pre-weighed vial where they were concentrated further under a gentle stream of N_2 until constant weight. HEL were calculated gravimetrically.

5.2.2 SPMDs

Semi-permeable membrane devices (SPMDs) have been used as time integrated monitoring systems to sample organic contaminants in the atmosphere of remote and less remote areas (Petty et al., 1993; Prest et al., 1995; Ockenden et al., 1998; Booij and van Drooge., 2001). SPMDs consist of a low-density polyester bag of 30cm length, 2.5cm wide, and with a wall thickness of 70 μm , which is filled with a natural lipid or the modified lipid triolein (1,2,3-tri[cis-9-octadecenoyl]glycerol). Exposed to the atmosphere they absorb organic contaminants from the gas phase. Since the PCBs and HCB in the high-mountain atmosphere are predominantly situated in the gas phase, SPMDs can be used to measure their levels in the atmosphere over a period of months.

The uptake is governed by

$$N_s = C_a K_{sa} V_s (1 - \exp[-k_e t]) \quad (1)$$

where N_s is the absorbed amount of contaminant in the SPMD, C_a is the concentration in the atmosphere, K_{sa} is the SPMD-air partitioning coefficient, V_s is the volume of the SPMD, k_e is the uptake rate and t is the exposure time. k_e is defined as

$$k_e = k_o A / k_{sa} V_s \quad (2)$$

where A is the exposure surface and k_o is the overall mass transfer coefficient, which is defined as

$$k_o^{-1} = (k_m K_{ma})^{-1} + k_a^{-1} \quad (3)$$

where k_m , k_a are the mass transfer coefficients for the membrane and for the air boundary layer, and k_{ma} is the membrane-air partitioning coefficient. So, the concentrations in air can be calculated from

$$C_a = N_s / (K_{sa} V_s [1 - \exp(-k_e t)]) \quad (4)$$

The denominator in equation 4 can be interpreted as the effective air volume extracted by the SPMD during the exposure. The extracted air volume may differ between compounds because K_{sa} and k_e are compound-dependent.

When $k_e t \rightarrow 0$ (short exposure times), the term between brackets is close to zero. Moreover, equation 4 is not commonly used to calculate C_a . The usual method is to check for which compounds equilibrium is attained. For these compounds, C_a is calculated from the concentration in the SPMD and the SPMD-air partitioning coefficient (K_{sa}). For the compounds that have not attained equilibrium, a constant air-sampling rate is assumed. The $k_o A$ limit set for choosing either method is arbitrary, and it is not obvious what to do when compounds attain 30 or 70% of their equilibrium concentration. The advantage of equation 4 is that it covers both extremes, as well as the intermediate situation when partial equilibrium is attained. The limiting cases for short and long exposure times of this equation are as follow.

Equilibrium is attained when $k_e t \rightarrow \infty$ (long exposure times). Then, equation 4 reduces to

$$C_a = N_s / K_{sa} V_s \quad (5)$$

which states that the concentration in air can be calculated from the concentration in the SPMD ($N_s / V_s = C_s$) and the partitioning coefficient (K_{sa}).

The SPMD-air partitioning coefficient K_{sa} is temperature dependent and is calculated by

$$K_{sa} = K_{sw} RT/H \quad (6)$$

where K_{sw} is the SPMD-water partitioning coefficient obtained from Booij et al., (2003).

For small exposure times, the compounds are in the linear uptake mode. Making the Taylor series expansion of $\exp(-k_e t)$ around $k_e t = 0$

$$\begin{aligned} C_a &= N_s / K_{sa} V_s k_e t \\ &= N_s / R_s t \end{aligned} \quad (7)$$

which is the sampling rate equation, with

$$R_s = K_{sa} V_s k_e \quad (8)$$

Since there are only few data on sampling rates by SPMD, the uptake kinetics can be evaluated using the (first order) dissipation rate constant of performance reference compounds (PRCs), which can be calculated from

$$k_e = -\ln(N / N_0) / t \quad (9)$$

where N is the PRC amount remaining after the deployment, and N_0 is the amount that was initially present in the SPMD at $t = 0$. Usually, however, only a single PRC can be used to calculate k_e . Compounds with small K_{sa} values have completely dissipated, and there is nothing left to quantify. For compounds with high K_{sa} values, the decrease in amounts is often too small to quantify. When the exchange kinetics between air and SPMDs are controlled by the air boundary layer, some basic arguing can be used to calculate k_e values for all compounds from the measured k_e for one PRC. For boundary layer controlled uptake the overall mass transfer coefficient for the boundary layer ($k_o \approx k_a$)

$$k_e = k_a A / K_{sa} V_s \quad (10)$$

PRC-based exchange rate coefficients (k_{e1}) can be used to calculate the coefficients for other compounds (k_{e2}) using

$$k_{e2} = k_{e1} (K_{sa1} / K_{sa2}) (k_{a2} / k_{a1}) \quad (11)$$

There is general agreement in the literature that mass transfer coefficients for fluid boundary layers are inversely proportional to the 2/3 power of the molecular diffusion coefficient. Hence,

$$k_{e2} = k_{e1} (K_{sa1} / K_{sa2}) (D_{a1} / D_{a2})^{2/3} \quad (12)$$

The leading term in equation 12 is the ratio in SPMD-air partitioning coefficients, which may largely differ between compounds. The ratio of diffusion coefficients usually is quite small. For example, the difference in D_a between HCB and PCB#180 is only a factor of about 1.2.

Concentrations in air for all compounds may be calculated from the dissipation of a single PRC, provided that the exchange kinetics is boundary layer controlled. This condition may be relaxed for compounds that are more volatile than the PRC, because the PRC usually has attained some degree of equilibrium, and the more volatile compounds will have attained a larger degree of equilibrium, which allows for the application of equation 5 anyway.

For very short studies, where the extracted volume is too small to detect compounds in the SPMDs, or in studies of the gas- particulate phase partitioning, the passive sampling method with SPMDs is not useful. Here the conventional HiVol-sampler can be used. A drawback of the HiVol-sampler is that it needs electrical supply to pump air through the adsorption material. At remote sites, like high-mountain areas, this can only be done with the use of a generator. On the contrary, SPMDs are easy to handle, relatively cheap and can be exposed on any site, where they passively sample the atmosphere.

Figure 23. SPMD-sampler situated at Tuc deth Port de Vielha (2600m).

5.2.2.1 Sample collection and analytical procedure of SPMD

From March 2002 until June 2003 SPMDs were exposed to the atmosphere on the border of the high mountain lake Estany Redon (Central Pyrenees), and analysed on HCB and individual PCB congeners. Further more, pump samplings were performed simultaneously in the valley and on the mountain top, at 1600m and 2600m respectively, in the vicinity of Estany Redon (Figure 23).

SPMDs were exposed in duplicate during 3 sampling periods of 85, 161 and 210 days, between March 2002 and June 2003. The SPMDs were filled with 270mg spiked triolein (Sigma, 95%). Triolein was spiked with 40, 7, 7 ng of PCB#4, PCB#29 and PCB#155, respectively. None of these PCB appeared in the atmospheric samples. To protect the SPMDs against direct sunlight and wind they were hanged inside a sampler, which consists of an untreated wood pole with a zinc bucket upside down that was closed off with a steel wire screen. Similar samplers were used successfully in other studies (Booij and van Drooge, 2001). In all sampling periods two non-exposed SPMDs filled with spiked triolein were analysed as blank. Their amounts were subtracted from the exposed SPMDs.

The SPMDs were stored and transported in closed glass bottles at -20°C . A few hours before exposure and after exposure they were stored at 0°C . Handling of SPMDs was done with pre-cleaned tweezers. After exposure the exterior of the SPMDs were wiped off with a tissue in order to remove eventually attached particles. Then, after cutting off the (triolein free) mounting loops, the SPMDs were extracted twice for 24h with 100ml hexane:DCM (4:1 v/v). Internal standards, PCB#30 and PCB#209, were added at the beginning of the first extraction period. The analytical recovery was studied twice using SPMDs that contained PCB spiked triolein. For each series, 2 SPMDs were used as for control purposes.

All extracts were concentrated to 0.5 mL. Clean up of extract was done by using a 8 g silica (5% H_2O) + 8 g aluminium oxide (5% H_2O) + 1 g Na_2SO_4 column with 20 mL hexane and 20 mL hexane/DCM (19/1 v/v). The collected fraction was then evaporated until 0.5 mL using vacuum rotary evaporation and further concentrated until 50 μL in iso-octane under a gentle nitrogen stream.

5.2.3 Quantification of *Pinus uncinata* leaves and SPMD

Before injection 25 μL of tetrachloronaphthalene were added to the extracts to correct for variation in instruments and end volume. The extracts were injected into a gas chromatograph equipped with an electron capture detector (GC-ECD; Hewlett-Packard 5890 Serie II) for the analysis of HCB, PCB congeners #18, #28, #52, #101, #110, #153, #138, #180. The GC was equipped with a fused silica capillary column DB5 (50 m x 0.25 mm i.d. x 0.25 μm film thickness; J&W Scientific, Folsom, CA). Nitrogen and helium were used as make up gas (60 mL min^{-1}) and carrier gas (0.33 mL min^{-1}). The oven temperatures were programmed from 100°C (1 min) to 150°C at $15^{\circ}\text{C min}^{-1}$, following a heating of $4^{\circ}\text{C min}^{-1}$ until 240°C (holding time 12 min.), and then to

300°C at 4°C min⁻¹ with a final holding time of 10 min. Samples were injected in split/splitless mode at 280°C. The detector temperature was 310°C.

The external standard method was used for the identification of the peaks in the chromatograms corresponding to the different retention times of the compounds on the column and to quantify the OC. The concentration range of the external standards covered the range of compound concentrations found in the samples. The limit of quantification (LOQ) was calculated from the average blank value plus 3 times the standard deviation. Blank values of detected compounds were about 30-200pg. LOQs were between 100-500pg for analysed OC.

5.3 Soil

Soils on the Island of Tenerife, Estany Redon and Ladove Pleso were collected in 2001. All soil sample analyses were done by Dr. Sandra Ribes-Cartagena. The sampling and analytical procedure was the same for all samples.

5.3.1 Sample collection on Tenerife

On the island of Tenerife soil samples were collected on the north-eastern slopes at 26 different altitudes, from 10m up to 3400m. Prior to sample collection the fresh litter was removed. Then, between 19m and 2500m the upper 5cm of surface soils were collected with a soil corer. Samples above 2500m, who were very stony and dry, were sampled with a small shovel and shifted through 500µm. The samples wrapped in aluminium foil, packed in heat sealable polyester bags and stored at 4°C until analysis (Ribes et al., 2002).

5.3.2 Sample collection in high-mountains

In the Central Pyrenees (Estany Redon) and the High Tatra (Ladove Pleso) a 7 cm (diameter) x 20 cm (long) stainless steel cylinder was used for soil core collection. All soils were taken in the lake catchment areas. They were then immediately divided in sections of 2 and 0.5 cm, respectively, and stored in pre-cleaned aluminium foil at -20°C until analysis.

5.3.3 Analytical procedure of soil samples

Soils were weighted into a Whatman Soxhlet cellulose thimble. About 1:1 w/w sodium sulphate was mixed with the soil samples in order to improve Soxhlet extraction by water removal. Prior to extraction, samples were spiked with PCB congeners #30 and #209, which were used as surrogate standards. In Table 7 the recoveries of soil extraction method are presented. Samples were extracted with hexane:DCM (4:1 v/v) for 18 h. All extracts were first concentrated by rotary vacuum evaporation to 3-5mL and subsequently eluted through an anhydrous sodium sulphate column. After rotary vacuum evaporation to ~0.5mL, the extracts were fractionated on a neutral

aluminium oxide column (2g) and fractions were eluted with with 8mL of hexane:DCM (9:1 v/v) and 10mL of hexane:DCM (1:2). About 0.5g activated copper (size<63 μ m) (Merck, Darmstadt, Germany) were added to OC fraction. Copper powder was activated by sonification with 25% hydrochloric acid (3x 5mL) (Merck, Darmstadt, Germany) and then it was rinsed several times with Milli-Q water to neutral pH and, subsequently, with acetone for removal of water. After manual steering the suspensions were kept overnight at room temperature. This copper powder was removed by filtration through glass wool and rinsed with *n*-hexane. Elution solvent and rinses were concentrated to 50 μ L in isooctane after rotary vacuum and nitrogen stream evaporation.

5.3.4 Quantification of soil samples

The following OC were determined in the soil cores: PAH, HCB, α -HCH, β -HCH, γ -HCH, δ -HCH, DDTs and PCB congeners #18, 28, 52, 70, 101+90, 110, 149+123, 118, 153, 132+105, 138, 160+158, 180, 194 and 199. Identification and quantification of the organochlorine compounds were the same as the method used for the atmospheric samples (paragraph 5.1.5.1 and 5.1.5.2 for OC and PAH, respectively).

5.3.5 TOC in soils

Soil samples were extracted with HCl (3N) to remove the inorganic carbon. Subsequently, they were cleaned with Milli-Q water until neutral pH (7 ± 2) and dried at 60°C. The determination of total organic carbon (TOC) was performed by flash combustion at 1025°C followed by thermic conductivity detection in a CHNS Elemental Analyser EA1108. These analyses were done by the Laboratory for Micro-analysis (IIQAB-CSIC, Barcelona, Spain).

5.3.6 Black-carbon (BC)

Black carbon was determined by the chemo-thermal oxidation (CTO) method (Gustafson and Dickhut, 1997; Gustafsson et al., 2001). In this thesis BC refers to the measurements with this CTO method, which in some cases may be similar to the soot-carbon. The BC analyses were done by Dr. Örjan Gustafsson (ITM, Stockholm University, Sweden).

5.4 Sediments

The sediment cores of Estany Redon, Dlugi Staw and Starolesnianske Pleso have been sampled for the MOLAR project in 1996. The analyses were done by Dr. Pilar Fernandez and Dr. Rosa M. Villanova. The sediment core of Ladove Pleso was collected in September 2001 and analysed for the EMERGE project. In all cases the sampling and analytical procedures were the same (5.4.1). All samples were analysed on their TOC content and their age. The methodologies for TOC determination and core dating are presented in 5.4.3 and 5.4.4, respectively.

5.4.1 Sample collection and analytical procedure of high-mountain lake sediments

Samples were obtained by using a gravity coring system (Glew, 7.5cm diameter; 30cm long) for sediment coring in the deepest point of the lake. At shore, sediment cores were immediately divided in sections of 2 and 0.5cm, respectively (0.3 and 0.25cm in the case of Redon and Ladove sediments, respectively), and stored in pre-cleaned aluminum foil at -20°C until analysis in laboratory. Wet sediment sections were extracted by sonification with methanol (1x20mL; 20 min.) and, subsequently, with DCM-methanol (2:1 (v/v); 3x20mL; 20 min.). PCB#30 and PCB#209 standards, together with deuterated anthracene and benzo(ghi)perylene, were added to combined extracts. The recoveries of the surrogates are presented in Table 7. Then, the extracts were vacuum rotary evaporated until 10mL. They were hydrolyzed overnight with 20mL of 6% KOH (Panreac, Spain) in methanol. The neutral fractions were recovered with *n*-hexane (3x10mL), and vacuum rotary evaporated until 0.5mL. The extracts were then transferred to a glass column (35cm x 0.9 i.d) packed with 2g of activated aluminium oxide. OC were collected in the first fraction with 5 mL of *n*-hexane-DCM (19:1 (v/v)). PAH were collected in the second fraction with *n*-hexane-DCM (1:2 (v/v)). About 0.5g activated copper was added to OC fraction. Then the fraction was transferred to another flask. Both, OC and PAH fractions were vacuum rotary concentrated until 1 mL and further concentrated until 50 μL in iso-octane under a gently nitrogen stream. Extracts were stored at -20°C before injection in gas-chromatograph.

5.4.2 Quantification of sediment samples

In sediments, PAH, HCB, DDTs and the polychlorobiphenyl congeners #28, 52, 101+90, 149+123, 118, 153, 138 and 180 were determined. In addition, PCB congeners #70, 110, 132+105, 160+158, 194 and 199 were also analysed in the sediment core of Ladove Pleso. Identification and quantification of the organochlorine compounds was the same as the method used for the atmospheric samples (paragraph 5.1.5.1 and 5.1.5.2 for OC and PAH respectively).

5.4.3 TOC in sediments

Sediment samples were extracted with HCl (3N) to remove the inorganic carbon. Subsequently, they were cleaned with Milli-Q water until neutral pH (7 ± 2) and dried at 60°C . The determination of TOC was performed by flash combustion at 1025°C followed by thermic conductivity detection in a CHNS Elemental Analyser EA1108. These analyses were done by the Laboratory for Micro-analysis (IIQAB-CSIC, Barcelona, Spain).

5.4.4 Core dating

In 4.3.2 it was already mentioned that the chronology of sediment accumulation is estimated from the changes in concentrations of natural radioactivity. Sediment samples were analysed for ^{210}Pb , ^{226}Ra , ^{137}Cs and ^{241}Am by direct gamma assay using Ortec HPGe GWL series

well-type coaxial low background intrinsic germanium detectors (Appleby et al., 1986). ^{210}Pb was determined via its gamma emissions at 46.5 keV and ^{226}Ra by the 295 keV and 352 keV γ -rays emitted by its daughter isotope ^{214}Pb following 3 weeks storage in sealed containers to allow radioactive equilibration. ^{137}Cs and ^{241}Am were measured by their emissions at 662 keV and 59.5 keV. The absolute efficiencies of the detectors were determined using calibrated sources and sediment samples of known activity. Corrections were made for the effect of self absorption of low energy γ -rays within the sample (Appleby et al., 1992). Supported ^{210}Pb activity was assumed to be equal to the measured ^{226}Ra activity. Unsupported ^{210}Pb activity was calculated by subtracting supported ^{210}Pb from the measured total ^{210}Pb activity. ^{210}Pb radiometric dates were calculated using the CRS and CIC dating models (Appleby and Oldfield, 1978). These dates were validated against the 1986 and 1963 depths determined from the $^{137}\text{Cs}/^{241}\text{Am}$ stratigraphic records. The core datings were done by Dr. Peter Appleby (University of Liverpool, UK).

Table 7. Recoveries of surrogates in different sampling methods.

	PCB30	PCB209	Anthracene-d10	Benzo(ghi)perylene-d10
Atmosphere (gas)	$80 \pm 8\%$	$92 \pm 17\%$	$95 \pm 19\%$	$74 \pm 21\%$
(part.)	$73 \pm 10\%$	$83 \pm 16\%$	$89 \pm 14\%$	$68 \pm 28\%$
Deposition	$77 \pm 18\%$	$78 \pm 11\%$		
Pinus uncinata	$82 \pm 10\%$	$89 \pm 20\%$		
SPMD	$87 \pm 21\%$	$87 \pm 17\%$		
Soil	$70 \pm 14\%$	$95 \pm 25\%$	Na	$82 \pm 25\%$
Sediment	$69 \pm 11\%$	$82 \pm 11\%$	$65 \pm 14\%$	$79 \pm 18\%$

na = not analysed

Chapter 6 Results

Chapter 6. Results

The results of the accomplished studies in this PhD-thesis are presented here in the form of articles. Some of them are published in scientific journals, while others are submitted for publication. They include:

1. van Drooge, B.L., Grimalt, J.O., Torres-García, C.J., Cuevas, E., 2002, **Semivolatile organochlorine compounds in the free troposphere of the northeastern Atlantic**, *Environmental Science & Technology*, 36, 1155-1161.

Barend L. van Drooge: Sampling, analyses and interpretation

Joan O. Grimalt: Supervisor of PhD-thesis of BLVD, interpretation

Carlos J. Torres-García: Sampling, meteorological calculations, interpretations

Emilio Cuevas: Support with meteorological data, interpretation

2. van Drooge, B.L., Grimalt, J.O., Torres-García, C.J., Cuevas, E., 2001, **Deposition of semi-volatile organochlorine compounds in the free troposphere of the eastern North Atlantic Ocean**, *Marine Pollution Bulletin*, 42, 628-634.

Barend L. van Drooge: Sampling, analyses and interpretation

Joan O. Grimalt: Supervisor of PhD-thesis of BLVD, interpretation

Carlos J. Torres-García: Sampling, meteorological calculations, interpretations

Emilio Cuevas: Support with meteorological data, interpretation

3. Ribes, S., van Drooge, B., Dachs, J., Gustafsson, Ø., Grimalt, J.O., 2003, **Influence of soot carbon on the soil-air partitioning of polycyclic aromatic hydrocarbons**, *Environmental Science & Technology*, 37, 2675-2680.

Sandra Ribes: Sampling and analyses of soil samples, interpretation

Barend van Drooge: Sampling and analyses of air samples, interpretation

Jordi Dachs: Modeling of PAH soil-air partitioning, interpretation

Ørjan Gustafsson: Analyses of SC, interpretation

Joan O. Grimalt: Supervisor of PhD-thesis of SR and BLVD

4. van Drooge, B.L., Grimalt, J.O., Camarero, LL., Catalan, J., Stuchlík, E., Torres-García, C.J. Submitted. **Atmospheric semi-volatile organochlorine compounds in european high mountain areas (Central Pyrenees and High Tatras)**, Environmental Science & Technology.

Barend L. van Drooge: Sampling, analyses and interpretation

Joan O. Grimalt: Supervisor of PhD-thesis BLVD, interpretation

Jordi Catalan: Sampling in the Pyrenees, interpretation

Lluís Camarero: Sampling in the Pyrenees, meteorological data, interpretation

Evzen Stuchlík: Sampling in the High Tatras, meteorological data, interpretation

Carlos J. Torres-García: Calculation of air mass back-trajectories, interpretation

5. van Drooge, B.L., Grimalt, J.O. submitted. **PCBs in *Pinus uncinata*, the uppermost growing tree species of central pyrenean high mountains (Catalonia, Spain)**, Chemosphere

Barend L. van Drooge: Sampling, analyses and interpretation

Joan O. Grimalt: Supervisor of PhD-thesis BLVD, interpretation

6. van Drooge, B.L., Grimalt, J.O., Booij, K., Camarero, LL., Catalan, J. Submitted. **Passive sampling of atmospheric organochlorine compounds by SPMDs in a high-mountain area (Central Pyrenees)** Environmental Science & Technology.

Barend L. van Drooge: Sampling, analyses and interpretation

Joan O. Grimalt: Supervisor of PhD-thesis BLVD, interpretation

Kees Booij: Development of SPMD technique, interpretation

Jordi Catalan: Sampling, interpretation

Lluís Camarero: Sampling, meteorological data, interpretation

7. Grimalt, J.O., van Drooge, B.L., Ribes, A., Vilanova, R.M., Fernàndez, P., Appleby, P., 2004, **Persistent organochlorine compounds in soils and sediments of European high altitude mountain lakes**, Chemosphere, 54, 1549-1561.

Joan O. Grimalt: Supervisor of PhD-thesis of BLVD, AR and RMV, interpretation

Barend L. van Drooge: Analyses of Ladove Pleso, interpretation

Sandra Ribes: Analyses of soil samples, interpretation

Rosa M. Vilanova: analyses of Starolesnianske Pleso, Dlugi Staw and Estany Redon, interpretation

Pilar Fernàndez: Supervisor of PhD-thesis RMV, interpretation

Peter Appleby: Radiometric dating, interpretation

8. Grimalt, J.O., van Drooge, B.L., Ribes, A., Fernández, P., Appleby, P. Submitted. **Polycyclic aromatic hydrocarbon composition in soils and sediments of high altitude lakes.** Environmental Pollution

Joan O. Grimalt: Supervisor of PhD-thesis of BLVD and AR, interpretation

Barend L. van Drooge: Analyses of Ladove Pleso, interpretation

Sandra Ribes: Analyses of soil samples, interpretation

Pilar Fernández: analyses of Starolesnianske Pleso, Dlugi Staw and Estany Redon, interpretation

Peter Appleby: Radiometric dating, interpretation

9. van Drooge, B.L., Grimalt, J.O., Axelman, J., Gustafsson, Ø., Jones, K.C., Stephanou, E. Submitted. **Congener specific assessment of global atmospheric PCB pool.** Environmental Science & Technology.

Barend L. van Drooge: Analyses of atmospheric samples from Tenerife, interpretation

Joan O. Grimalt: Supervisor of PhD-thesis BLVD, interpretation

Johan Axelman: interpretation

Ørjan Gustafsson: interpretation

Kevin C. Jones: interpretation

Euripides Stephanou: interpretation

The presented results are discussed in Chapter 7 of this thesis, which is divided in three blocks.

- Atmospheric transport and fate of POP in the subtropical troposphere (article 1 – 3)
- Atmospheric transport and fate of POP in European high-mountain areas (article 4 – 8)
- Global atmospheric fate of POP with PCBs as model compounds (article 9)

