

Universitat Autònoma de Barcelona

Facultat de Ciències  
Programa de Doctorat de Ciències Ambientals  
Opció: Anàlisi del Medi Natural

**LONG-RANGE ATMOSPHERIC TRANSPORT  
AND FATE OF PERSISTENT ORGANIC  
POLLUTANTS IN REMOTE MOUNTAIN AREAS**

Barend L. van Drooge  
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A l'últim bes del sol ponent, blanqueja  
com un colom entre el fullatge verd;  
perquè de lluny algun pastor no el veja,  
de cortines de boira s'ha cobert.

Està enmig de l'estany com una estrella  
florida enmig del cel de juliol,  
nimfea colossal que s'esbadella  
al bes de les escumes i del sol.

Per ses arrels lo lliguen a la vora,  
com branques de coral esblanqueït,  
quatre ponts de cristall del que atresora  
la serra en ses entranyes de granit.

(fragment from El Canigó, Jacint Verdaguer (1885))

For Ingrid.

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**Index**

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**Index**

<b>Samenvatting</b>		<b>7</b>
<b>Resum</b>		<b>8</b>
<b>Chapter 1</b>	<b>Introduction and Objectives</b>	<b>11</b>
1.1	Global Environmental Changes	11
1.2	Objectives of the PhD-thesis	13
<b>Chapter 2</b>	<b>Persistent Organic Pollutants (POP)</b>	<b>17</b>
2.1	Organochlorine Compounds (OC)	17
2.1.1	OC pesticides	17
2.1.1.1	4,4'-DDT and 4,4'-DDE	18
2.1.1.2	HCHs	19
2.1.1.3	HCB	20
2.1.1.4	Endosulphanes	20
2.1.2	Industrial OC: Polychlorinated biphenyls (PCBs)	21
2.2	Polycyclic Aromatic Hydrocarbons (PAH)	23
<b>Chapter 3</b>	<b>Sampling sites in high-mountain areas</b>	<b>29</b>
3.1	Subtropical troposphere	31
3.1.1	The Island of Tenerife	31
3.1.2	Soils and vegetation	31
3.1.3	Meteorological conditions	32
3.1.4	Human activity	34
3.2	European high-mountain areas	35
3.2.1	Central Pyrenees: Estany Redon	36
3.2.1.1	Geographical situation and origin of Estany Redon	36
3.2.1.2	Geomorphology, soils and vegetation	37
3.2.1.3	Meteorological conditions	38
3.2.1.4	Human activity	39
3.2.2	The High Tatras	39
3.2.2.1	Geographical situation and origin of the studied lakes	39
3.2.2.2	Geomorphology, soils and vegetation	40
3.2.2.3	Meteorological conditions	40
3.2.2.4	Human activity	41
<b>Chapter 4</b>	<b>Atmospheric transport and fate of POP in remote mountain areas</b>	<b>45</b>
4.1	Atmospheric dynamics of POP	46
4.2	Atmospheric removal pathways	47
4.2.1	Photo-degradation	47

---

4.2.2	Deposition	49
4.2.2.1	Wet deposition	50
4.2.2.2	Dry deposition	50
4.2.2.3	Gas exchange	51
4.2.3	Atmospheric Persistence and Long-Range Transport	52
4.3	Retention of POP in soils and sediments	55
4.3.1	POP in remote soils	55
4.3.2	POP in remote lake water and sediments	57
4.4	Environmental fate of POP in remote high altitude areas	58
<b>Chapter 5</b>	<b>Methods and Materials</b>	<b>63</b>
5.1	Atmosphere	63
5.1.1	Atmospheric gas and particulate phase	64
5.1.2	Back-trajectories of air masses	65
5.1.3	Atmospheric temperatures ( $T_a$ )	65
5.1.4	Atmospheric deposition	65
5.1.5	Quantification of atmospheric samples	66
5.1.5.1	Identification and quantification of OC	66
5.1.5.2	Identification and quantification of PAH	67
5.2	<i>Pinus uncinata</i> and SPMD	67
5.2.1	<i>Pinus uncinata</i>	68
5.2.1.1	Sample collection and analytical procedure of <i>Pinus uncinata</i> leaves	69
5.2.1.2	Dry weight and hexane-extractable lipid content	69
5.2.2	SPMDs	69
5.2.2.1	Sample collection and analytical procedure of SPMD	73
5.2.3	Quantification of <i>Pinus uncinata</i> leaves and SPMD	73
5.3	Soils	74
5.3.1	Sample collection on Tenerife	74
5.3.2	Sample collection in high-mountains	74
5.3.3	Analytical procedure of soil samples	74
5.3.4	Quantification of soil samples	75
5.3.5	TOC in soils	75
5.3.6	Black-carbon (BC)	75
5.4	Sediments	75
5.4.1	Sample collection and analytical procedure of high-mountain lake sediments	76
5.4.2	Quantification of sediment samples	76
5.4.3	TOC in sediments	76
5.4.4	Core dating	76



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<b>Chapter 6</b>	<b>Results</b>	<b>81</b>
Article 1.	Semivolatile organochlorine compounds in the free troposphere of the Northeastern Atlantic	85
Article 2.	Deposition of semi-volatile organochlorine compounds in the free troposphere of the eastern North Atlantic Ocean	95
Article 3.	Influence of soot carbon on the soil-air partitioning of polycyclic aromatic hydrocarbons	105
Article 4.	Atmospheric semi-volatile organochlorine compounds in European high mountain areas (Central Pyrenees and High Tatras)	113
Article 5.	PCBs in <i>Pinus uncinata</i> , the uppermost growing tree species of Central Pyrenean high mountains (Catalonia, Spain)	133
Article 6.	Passive sampling of atmospheric organochlorine compounds by SPMDs in a high-mountain area (Central Pyrenees)	147
Article 7.	Persistent organochlorine compounds in soils and sediments of European high altitude mountain lakes	163
Article 8.	Polycyclic aromatic hydrocarbon composition in soils and sediments of high altitude lakes	179
Article 9.	Congener specific assessment of global atmospheric PCB pool	201
<b>Chapter 7</b>	<b>Discussion</b>	<b>229</b>
7.1	Atmospheric transport and fate of POP in the subtropical troposphere	229
7.1.1	Organochlorine compounds	229
7.1.2	Polycyclic aromatic hydrocarbons	230
7.2	Atmospheric transport and fate of POP in European high-mountain areas	231
7.2.1	Organochlorine compounds	231
7.2.1.1	Active air sampling: HiVol	231
7.2.1.2	Passive air sampling:	232
7.2.1.2.1	<i>Pinus uncinata</i>	232
7.2.1.2.2	SPMDs	233
7.2.1.3	Fate of OC in soils and lake sediments	233
7.2.2	Fate of polycyclic aromatic hydrocarbon in soils and sediments	237
7.3	Global atmospheric fate of POP with PCBs as model compounds	239
<b>Chapter 8</b>	<b>Conclusions</b>	<b>243</b>
<b>Bibliography</b>		<b>247</b>



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## Samenvatting

Persistente organische contaminanten (POP), zoals HCB, PCBs, DDTs, HCHs endosulfanen en PAKs, zijn wijd verspreid over het aardoppervlak. De meeste componenten zijn ooit gesynthetiseerd ten bate van de menselijke ontwikkeling, zonder in eerste instantie rekening te houden met de hun weerstand tegen biologische, chemische en fysieke degradatie, accumulatie in organisch materiaal en toxiciteit.

In de gepresenteerde studie wordt de rol getoetst van de atmosfeer in de distributie van POP in afgelegen berggebieden, en ook het lot van deze componenten in bodem en sedimenten van hooggebergtemeertjes. De POP niveaus in de subtropische troposfeer van Tenerife en de Europese hooggebergten van de Centrale Pyreneeën en de Hoge Tatras zijn aan de lagere zijde van de waarden die elders gevonden worden. Op alle monsternamenpunten zijn de meeste POP goed door de atmosfeer gemengd, wat duidt op het belang van atmosferisch transport over lange afstand. Naast actieve lucht monsternamen m.b.v. een HiVol-monsternamenapparaat is er passieve monsternamen van lucht toegepast in de vorm van dennennaalden van de *Pinus uncinata* en half-doorlaatbare membranen (SPMDs) voor de studie van de ruimtelijke en tijdelijke distributie van organische chloorverbindingen in de Centrale Pyreneeën.

De lucht-bodem verdeling van PAKs op Tenerife geeft het belang aan van roet koolstof in de transfer van PAKs naar de plaatsen boven de inversielaag. Ook in de Europese hooggebergten worden de POP in de bodem goed weergegeven door de POP in de aerosols. Desalniettemin worden POP beter behouden in de sedimenten van de hooggebergtemeertjes. Verticale profielen van de sedimenten tonen een significante toename van POP niveaus aan het eind van de tweede helft van de 20<sup>ste</sup> eeuw, wanneer de productie en gebruik van deze componenten op gang komt, en een significante afname vindt plaats in de laatste jaren, wat een contributie kan zijn van de het beleid op schonere lucht en verbeterde verbrandingstechnieken.

Een model voor atmosferische PCB congeners op wereldschaal is verder geformuleerd. Dit model evalueert de degradatie van PCBs door OH-radicalen en hun geschatte troposferische verblijftijden.

Alle vermelde resultaten in deze thesis zijn gepresenteerd in de vorm van wetenschappelijke artikelen die gepubliceerd staan, ter perse liggen, of gereценееrd worden voor publicatie.

## Resum

Els compostos orgànics persistents (COPs) com l'HCB, els PCBs, els DDTs, els HCHs, els endosulfans i els HAPs, són contaminants ubiqües distribuïts per tot el planeta. La majoria d'ells foren sintetitzats per beneficiar el desenvolupament humà, sense tenir en compte la seva resistència a les degradacions biològiques, químiques i físiques, la seva capacitat d'acumulació en material orgànic i la seva toxicitat.

En la present memòria de tesi s'estudia el paper de l'atmosfera en la distribució ambiental dels COPs en les àrees remotes de muntanya i els destí d'aquests compostos en els sòls i els sediments dels llacs d'alta muntanya. S'han estudiat els COPs en la troposfera subtropical de Tenerife i l'atmosfera de l'alta muntanya europea (Pirineus centrals i Tàtres altes) es troben dins del marge inferior dels observats en altres atmosferes remotes. En tots els llocs d'estudi, la majoria de COPs estan ben homogeneïtzats dins l'atmosfera, tot indicant la importància del transport atmosfèric a llargues distàncies (LRAT) com a mecanisme principal de transferència d'aquests compostos cap a les zones remotes. A part d'un mostratge actiu amb l'aparell HiVol, s'ha realitzat un mostratge passiu de l'atmosfera amb fulles de *Pinus uncinata* i amb membranes semipermeables (SPMDs), que ha permès estudiar la distribució espacial i temporal dels compostos organoclorats en els Pirineus centrals.

La partició aire-sòl dels HAPs a Tenerife mostra que el sutge és el factor principal en la transferència de HAPs als sòls per sobre la capa d'inversió. L'alta muntanya europea també mostra una bona correlació entre les concentracions de COPs en els sòls i els aerosols. De tota manera, els COPs es conserven millor en els sediments dels llacs. Els perfils sedimentaris verticals mostren un augment significatiu dels nivells de COPs a finals de la segona meitat del segle XX, quan la producció i l'ús d'aquests compostos començava, i una disminució en els últims anys, probablement deguda a la contribució de les polítiques de control de la qualitat de l'aire i a la millora de les tècniques de combustió.

Addicionalment, en aquesta tesi s'ha formulat un model de distribució atmosfèrica dels congèneres de PCBs a escala global que pren consideració dels fenòmens de degradació d'aquests compostos per radicals OH i del temps de residència estimat dels PCBs en l'atmosfera.

Tots els resultats esmentats es presenten en forma d'articles científics que ja han estat publicats o estan en procés de publicació.

## **Chapter 1    Introduction and Objectives**

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## Chapter 1 Introduction and Objectives

### 1.1 Global Environmental Changes

Since the beginning of human development, the anthropogenic activities (hunting, burning of wood, agricultural activities, etc.) have left their mark on the environment. Nowadays, the increase and intensification of activities related to the industrialised society, with its unlimited demand and use of energy, have resulted in the environmental effects that are not anymore punctual and on local scale (near to the sites of production or/and application). The accumulation of effects due to human activities is generating global environmental changes. These processes can be observed in the presence of toxic compounds in the environmental compartments (water, soils and atmosphere) and its organisms, from remote environments, like the Polar regions and high-mountains areas (AMAP 1998; Grimalt et al.2001). Under the concept of Global Environmental Changes one can include problems like global climate change, destruction of the ozone layer, irreversible loss of biodiversity, desertification, acidification, and contamination of air, water, soils and organisms due to human activities. The chemical substances responsible for many of these problems can be defined as global contaminants and they include among others:

- CO<sub>2</sub>, CH<sub>4</sub> and other greenhouse gasses.
- SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and other compounds causing acid rain.
- Chlorofluorocarbons (CFC) and other gasses that destroy the ozone layer.
- Radioisotopes, like <sup>137</sup>Cs, <sup>14</sup>C, and <sup>90</sup>Sr, generated during nuclear trials.
- Heavy metals, like mercury and lead.
- Persistent organic pollutants (POP), like the polycyclic aromatic hydrocarbons (PAH) and the semi-volatile organochlorine compounds (SOC), such as polychlorinated biphenyls (PCB), DDT, hexachlorohexanes (HCH), hexachlorobenzenes (HCB), and endosulphanes.

The environmental effects caused by the POP are a direct consequence of their toxicity, stability and resistance against physical, chemical, or biological degradation. Most of the studied compounds, except PAH, are man-made or xenobiotic. They did not appear in the environment until men made them. Since the '40s of the 20<sup>th</sup> century, when the production and use started, these very useful compounds have been introduced in large quantities to the environment, where they have caused unforeseen harm. The intensification of the industry in the last century has increased the input of PAH to the environment to levels that have seriously affected the environmental health. It took until the late '60s when the negative effects of organochlorine compounds were acknowledged. Nevertheless, it was already at the beginning of the '60s that Rachel Carson rang the alarm bell in her thriller 'Silent Spring' about the unlimited use of these compounds (Carson, 1962). Although her book lacks in scientific evidences, later investigations proved quite well most of her worries. In the last decades many POP have been banned in most industrialised countries.

Accordingly, decreases of levels have been observed in potential source areas where the chemicals were produced and used (Rapaport and Eisenreich, 1988; Eisenreich et al., 1989; Jeremiason et al., 1994; Gobas et al., 1995; Kjeller and Rappe, 1995; Sanders et al., 1995). However, these compounds are still omnipresent in the environment and the observed decreases in remote areas are small if any (Baker and Eisenreich, 1990; Panshin and Hites, 1994; Hillery et al., 1997; Hung et al., 2001). Due to the specific environmental dynamics of POP, classical concepts like, 1) decrease of environmental impact with increasing distance from source, 2) dilution effect once entering into the open environment, such as the atmosphere or water bodies, and 3) long-range transport increases dilution, may **not be true** for these compounds. The physico-chemical properties of POP may offer a net transference of the pollutants from sites where they were produced or applied, to sites where they were never used, without undergoing any important form of dilution. Several studies in the past decades have shown that POP are ubiquitous pollutants (Atlas and Giam, 1980; Iwata et al., 1993). Moreover, due to the semi-volatile character they tend to accumulate in areas of low ambient temperatures, such as the Polar and high-mountain regions (AMAP 1998; Grimalt et al., 2001) (Chapter 4).

This is of concern since most of the compounds cause toxic effects (Porta et al., 1999; Vreugdenhil et al., 2002) (Chapter 2). The United Nations have recently elaborated a programme on POP, which was also signed by the European Union (UNEP/GC 18/32, 1995, Aarhus (Denmark) 1998 in Stockholm (Sweden) 2001; Bulletin EU 5-2001: 1.4.41). In this programme they compel themselves to reduce or eliminate the production of certain POP, to prohibit their use, and to investigate the effects on the environment and human health. So, in less than 60 years after the first application strict regulations have been implemented to eliminate POP from the environment. The scientific community has the responsibility to clarify where the diffuse emission sources of POP are located, what their impact is on remote fragile ecosystems, where they will end up, and how long they will be in the environment. These investigations can help policy making upon them and other chemical compounds in the future, since it may be possible to point out the consequences of production and use of chemicals and to provide suggestions for prevention of their adverse effects.

The study of these compounds in remote high-mountain areas, where no application ever took place, makes it possible to improve the understanding of their global transport and environmental fate (Chapter 3 and 4). High-mountain areas are vulnerable to POP contamination because of

- 1) long residence times of persistent and lipophilic compounds in these oligotrophic systems,
- 2) low volatility in cold climates,
- 3) thinner soil layers than in temperate and tropical areas,
- 4) slow biodegradation in soils and sediments due to low temperatures,
- 5) low sedimentation in lakes because of low annual primary production involving pollutant concentration thin sediment layers,

- 6) low species density, short food chains, and long lived animals in the top of the food chains which accumulate highly lipophilic contaminants in their bodies.

In the present study the role of the atmosphere in the distribution of POP in remote high-mountain areas is examined as well as the fate of these compounds in soils and lake sediments from these areas. Here fore, atmospheric, soil and sediment samples were collected and analysed in high-mountain areas from subtropical and temperate latitudes (Chapter 5). The atmosphere and atmospheric deposition data offered information on the transfer mechanisms of POP to these areas, while data from soil and sediment cores shows the historical input of the compounds. Both types of data sets are used to interpret the past and present degree of contamination of these remote mountain environments, and to interpret the interactions between the environmental compartments in these remote high-mountain sites (Chapter 6 and 7).

The studies presented in this thesis are part of larger European Community research projects dealing with the global transport and fate of POP (GLOBAL-SOC: *Global Mass Balance of Persistent Semi-volatile Organic Compounds*, project No: ENV4-CT97-0638) and the general environmental state of high-mountain lake areas (EMERGE: *European Mountain Lake Ecosystems: Regionalisation, Diagnostics and Socio-economic Evaluation*, project No: ENK1-CT1999-0032, <http://www.mountain-lakes.com>).

## 1.2 Objectives of the PhD-thesis

- 1) To measure and interpret the atmospheric background levels of POP in remote high-mountain areas on subtropical and temperate latitudes.
- 2) To measure and interpret the background levels of POP in soils and lake sediments from these areas.
- 3) To elucidate the mechanisms for the transport and fate of POP in remote high-mountain areas.
- 4) To understand the actual state of POP contamination on a regional and global scale.





## **Chapter 2    Persistent Organic Pollutants (POP)**

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## Chapter 2. Persistent Organic Pollutants (POP)

As mentioned already in the introduction POP are toxic chemical compounds, which are widespread over the world surface, becoming ubiquitous pollutants. However, each group of these compounds was manufactured for different purposes, used preferentially in different locations and has specific physico-chemical properties that have resulted in distinct distribution patterns. In this chapter the studied compounds are described. *A priori*, they can be separated in two groups. The man-made organochlorine compounds (see 2.1) and the natural polycyclic aromatic hydrocarbons (see 2.3).

### 2.1 Organochlorine Compounds (OC)

OC are man-made toxic chemical compounds that encompass a wide range of chemical compounds with different structures and purposes. Here, only two groups are described: pesticides and industrial products.

OC pesticides (see 2.1.1) were initially produced to protect crops and human beings. Their input to the environment corresponds to the times related to their application in agriculture, and is often related to the crop growing season and pest outbreaks. Nevertheless, these products can also enter into the environment when they are not stored adequately.

Industrial OC (see 2.1.2), here only polychlorinated biphenyls, were produced to be used, for example, as dielectric fluids and flame retardant materials in industrial processes and products. Their input to the environment was often related to diffusion into the atmosphere or seepage to groundwater after application.

Despite these different origins and uses both OC types have in common their resistance against physical, chemical and biological breakdown. In addition, their high number of chlorine atoms make them highly soluble in lipids and less soluble in water, tending to accumulate in body tissue. The persistence and toxicity of these compounds depend on the amount of chlorine atoms and their position in the molecule. During 1970s most western countries (where most of the products were produced and used) started to ban the manufacture and use of most of these compounds. Nevertheless, present use in closed installations, inadequate storage or waste-dumps still form potential sources of these toxic compounds for entering the environment. Nowadays, most of them are classified by the United Nations as Persistent Organic Pollutants (POP), (UNEP/GC 18/32, 1995 and <http://www.chem.unep.ch/pops/>).

#### 2.1.1 OC pesticides

OC pesticides were produced as insecticides, acaricides or nematicides for the protection of agriculture crops and human beings, but their persistence and non-species specificity caused several adverse effects in non-target species. The application of pesticides is often directly related to the

growing season of crops, or the pest outbreak. In this way the usage of pesticides is often season-related. The use of most of these products is nowadays prohibited, but they are still present in the environment. The following description of OC pesticides focus on the compounds that have been detected in the samples presented in this PhD-thesis.

#### 2.1.1.1 4,4'-DDT and 4,4'-DDE

Technical DDT (dichloro-diphenyl-trichloro-ethane) consists of more than 70% of the *para, para*- (4,4')-isomer and less than 30% of the *ortho, para*-isomer (Niesink et al., 1996). DDT was synthesised in 1874, but its "benefit" for crop protection was discovered in the late 1930s, leading to a Nobel Prize in 1948 for Paul Müller (Carson, 1962). The chemical was used since then for all kinds of purposes. It enters rapidly the cuticula of the insect where it provokes a violent stimulation of nerve impulses that eventually causes death. By the end of the 1960s it was realised that this chemical, and its metabolites DDD and DDE, were present in considerable levels in non-target species, causing serious toxic effects (Jensen 1966; Jensen et al., 1969). Especially the *para,para* (4,4') configuration of this family (Figure 1) is held to be responsible for the adverse effects.

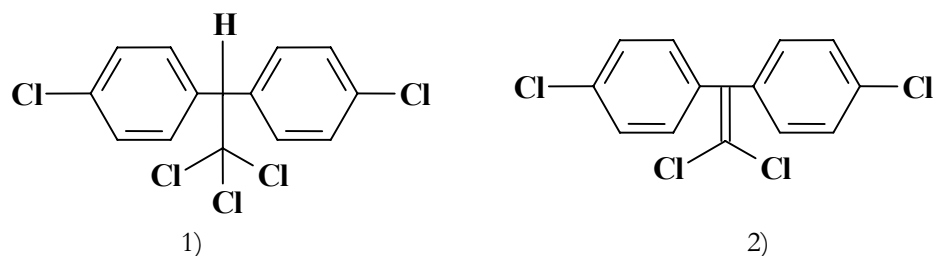


Figure 1. Molecular structures of 1) 4,4'-DDT and 2) 4,4'-DDE

DDTs are easily assimilated by organisms and adsorbed by soils and sediments, due to their high solubility in lipids, low solubility in water and high stability. DDE is more persistent than its parent DDT, and is still found in considerable amounts in high trophic levels and sediments in remote sites (Iwata et al., 1993; Newton, 1979). It is related to eggshell thinning, embryo-toxicity and failures in reproductive success of birds. For instance the peregrine falcon (*Falco peregrinus*) is considered to be very sensitive for DDE in its reproductive success (Newton, 1979; Steidl et al., 1991).

In the last 20 years many countries have banned the use of DDT by law, but in some parts of the world, like in many African countries, India and Mexico, it is still used as pest control for human diseases, like malaria and locusts pest (Douthwaite, 1991). Recently, a relationship was found between the exposure of 4,4'-DDE and 4,4'-DDT and the mutation of the K-ras gene in exocrine pancreatic cancer patients (Porta et al., 1999). Some physico-chemical properties of DDTs are summarised in Table 3.



### 2.1.1.3. HCB

HCB (hexachlorobenzene) (Figure 3) was used mainly as fungicide in wood and seed for crop production. However, it is also a by-product of several chlorinating procedures in manufacture of organochlorine solvents and can be found in plastics. Total estimated global emission is 23.000 kg yr<sup>-1</sup> with a range between 12.000 – 92.000 kg yr<sup>-1</sup> (Bailey, 2001).

It is almost insoluble in water, but evaporates very rapidly after release. Due to the high vapor pressure it is preferably found in the atmosphere where it can be transported over long distances. Nowadays this compound is banned, but is still delivered to the environment as by-product. HCB has shown to be acute toxic for men when in Turkey, between 1955 and 1959, it caused an outbreak of *porfiria cultanea tarda* after intake of contaminated food. Further on, there is a relationship between thyroid cancer and chronic exposure of HCB (Grimalt et al., 1994). Some physico-chemical properties of HCB are summarised in Table 3.

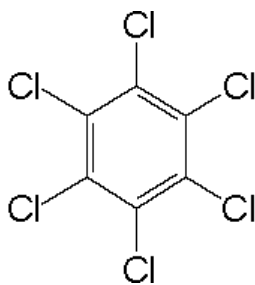


Figure 3. Molecular structure of HCB

### 2.1.1.4. Endosulphanes

Endosulphane, also known as thiodan, is an insecticide used in a wide range of applications to protect cereals, coffee, cotton, fruit, oilseed, potatoes, tea and vegetables against 'vandalism' of insects. The technical mixture contains approximately 70%  $\alpha$ -endosulphane (also called endosulphane-I) and 30%  $\beta$ -endosulphane (also called endosulphane-II) (Figure 4). As a consequence of this composition and the physico-chemical properties, the  $\alpha$ -isomer is more abundant in the environment than the  $\beta$ -isomer and is easily transported through the atmosphere. The oral LD<sub>50</sub> for technical endosulphane ranges between 18 and 355 mg kg<sup>-1</sup> body weight, which makes it one of the most toxic chlorinated insecticides. In 1988, the world's production of technical endosulphane was about 10.000 t yr<sup>-1</sup>. Because of its semivolatility (vapor pressure = 6.2 x 10<sup>-3</sup> Pa) and photolytical stability in water, endosulphane is ubiquitous in the environment (Burgoyne and Hites, 1993). Some physic-chemical properties of these compounds are listed in Table 3.

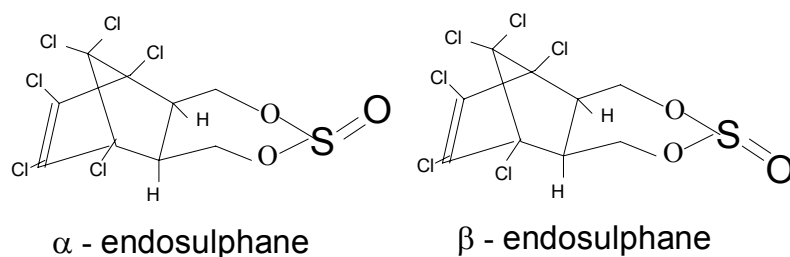


Figure 4. Molecular structure of  $\alpha$ - and  $\beta$ -endosulphane.

### 2.1.2 Industrial OC: Polychlorinated biphenyls (PCBs)

PCBs were industrial compounds used as industrial fluids, dielectric fluids, heat transfer fluids, organic solvents, flame retardants, plasticizers, sealants and surface coatings. Between 1930 and 1975 around 635.000 t were produced in the United States. Worldwide production is estimated to be 1.3 million t. of which 97% was used on the Northern Hemisphere (Breivik et al., 2002).

In commercial PCB mixtures, the amount of chlorine atoms in the biphenyls depends on the duration and the temperature of the chlorination process. After purification the mixtures were commercialised under different names. For example, Arochlor (Monsanto, USA) or Clophen (Bayer, EU). The chlorine atoms can substitute the *para*, *meta* and/or *ortho* positions of the biphenyls. There are 209 congeners that contain two phenyl groups and one or more chlorine substituents. In this way PCBs can be divided into nine isomeric groups and one deca-chlorobiphenyl, all with an empirical formula of  $C_{12}H_{10-n}Cl_n$  ( $n=1-10$ ) (Figure 5; Table 1). Some physico-chemical properties of PCBs are summarised in Table 3.

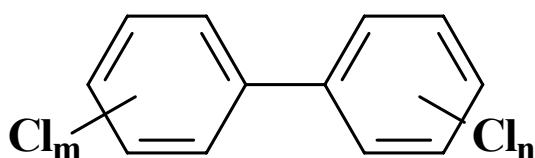


Figure 5. General molecular structures of PCBs.

PCBs were found for the first time in the environment by Sören Jensen, who detected the contaminants in pike from Swedish waters (Jensen, 1966). Within few years the adverse effects in organisms were recognised. Then their use and production were reduced (Safe, 1991, de Voogd et al., 1990) and finally banned in late 1970s in most industrialised countries.

PCBs are discharged into the environment by leaks from hydraulic, or industrial systems, diffusion out of coatings, or other products during production, waste incineration, or disposal, or after accidents. The levels of individual congeners differ from location and environmental compartment. Atmospheric PCBs are present predominately in the gas phase. However, the more chlorinated congeners are also present in the particulate phase (Pankow, 1987). There are evidences

that atmospheric PCBs are degraded by OH-radical reaction (Anderson and Hites, 1996a). However, the degradation rates under environmental conditions have not been determined to date. The study of these contaminants in remote atmospheres, such as the free-troposphere or high-mountain areas, may give insight into this question.

Table 1. Summary list of PCB congeners <sup>o)</sup> (Guitart et al., 1993; de Voogd et al., 1990)

Structural formula	Name (chloro biphenyl)	N <sup>o</sup> of isomers	IUPAC systematic numbering	Mol. wt	% Cl	N <sup>o</sup> of isomers identified in commercial mixtures
C12H9Cl	Mono	3	1-3	188.65	18.79	3
C12H8Cl <sub>2</sub>	Di	12	4-5	233.10	31.77	12
C12H7Cl <sub>3</sub>	Tri	24	16-39	257.54	41.30	23
C12H6Cl <sub>4</sub>	Tetra	42	40-81	291.99	48.65	41
C12H5Cl <sub>5</sub>	Penta	46	82-127	326.43	54.30	39
C12H4Cl <sub>6</sub>	Hexa	42	128-169	360.88	58.93	31
C12H3Cl <sub>7</sub>	Hepta	24	170-193	395.32	62.77	18
C12H2Cl <sub>8</sub>	Octa	12	194-205	429.77	65.98	11
C12HCl <sub>9</sub>	Nonta	3	206-208	464.21	68.73	3
C12Cl <sub>10</sub>	Deca	1	209	498.66	71.10	1

o) the corrected Ballschmiter and Zell nomenclature (Guitart et al., 1993) is used throughout the whole report.

Table 2. Selected PCB congeners

N <sup>o</sup>	Molecular structure
18	2,2',5-triCB
28	2,4,4'-triCB
52	2,2',5,5'-tetraCB
70	2,3',4',5-tetraCB
90	2,2',3,4',5-pentaCB
101	2,2',4,5,5'-pentaCB
105	2,3,3',4,4'-pentaCB
110	2,3,3',4',6-pentaCB
118	2,3',4,4',5-pentaCB
123	2,3,4,4',5-pentaCB
132	2,2',3,3',4,6'-hexaCB
138	2,2',3,4,4',5-hexaCB
149	2,2',3,4',5',6'-hexaCB
153	2,2',4,4',5,5'-hexaCB
158	2,3,3',4,4',6-hexaCB
160	2,3,3',4,5,6-hexaCB
180	2,2',3,4,4',5,5'-heptaCB
194	2,2',3,3',4,5,5',6'-octaCB
199	2,2',3,3',4,4',5,5'-octaCB

The position of the chlorine atoms in the molecule is important for PCB toxicity. They are more toxic when the *ortho* positions of the molecule are not substituted, e.g. PCB#77 (3,3',4,4'-tetraCB), PCB#126 (3,3',4,4',5-pentaCB) and PCB#169 (3,3',4,4',5,5'-hexaCB). In these conditions the two phenyl groups can freely rotate and align following a flat structure (planar or coplanar PCBs). *Mono-ortho* and *di-ortho* PCBs (with the 2 and 2' positions substituted) are less toxic (de Voogd et al., 1990). Reported biological effects on terrestrial animals exposed to PCBs involve liver



damage, dermal disorders (chloracne), reproductive toxicity, thymic atrophy, body weight loss, immunotoxicity and teratogenicity and induction of several cytochrome P-450 (enzyme) isozymes (de Voogd et al., 1990). Although the application of these products is restricted or prohibited for many years now, they still cause toxic effects at trace level, as shown a study on Dutch school children (Vreugdenhil et al., 2002). The 19 PCB congeners selected for study in the context of the present PhD-thesis are reported in Table 2. These congeners are representative for the overall PCB abundance in the different environmental compartments. Some physico-chemical properties of these compounds are summarised in Table 3.

## 2.2 Polycyclic Aromatic Hydrocarbons (PAH)

PAH are compounds that consist of C and H atoms, grouped in the form of fused benzene rings. They are generally produced in all sorts of combustion encompassing from fossil fuels, to organic materials, such as vegetation. PAH composition depends on the combusted organic material and the temperature at which combustion takes place (Howsam and Jones 1998). Larger molecules of high molecular weight are easily generated at lower temperatures due to lower combustion efficiencies. Thus, combustion of diesel oil produces relatively higher molecular weight PAH than gasoline in vehicular engines (Khalili et al., 1995). In the late 19<sup>th</sup> century and early 20<sup>th</sup> low temperature coal combustion was the major source of PAHs. Nowadays fossil fuels, like gas, are used, which generate less PAHs. Diagenetic processes produce PAH as well. But their contribution is of smaller importance than pyrolytic sources on the global PAH concentration.

PAH enter primarily into the environment by atmospheric emissions, and are atmospherically transported easily over long distances. In this way they become ubiquitous contaminants arriving to remote areas where they are not produced (Wania and Mackay, 1996), but may cause damage to the ecosystem. Some PAH and their metabolites are tetraoxygenated and mutagenic, like benzo[a]pyrene (Howsam and Jones 1998). Increases in the PAH concentrations in remote European high mountain lake sediments since the late 19<sup>th</sup> century reflect the increase of fossil fuel combustion due to intensification of industrial activities. In these lakes PAH exhibited highest concentrations between 1960 and 1980 and stabilised after 1980s (Fernández et al., 2000), probably caused by the effect of legislative restrictions and improvements in combustion technology.

In late 1970s the United States Environmental Protection Agency (USEPA) listed 16 PAH as 'Priority Pollutants'. This list was later adopted by the European Union. However, a much larger number of PAH are emitted to the environment in combustion processes, but research on the emissions and environmental fate of PAH has tend to focus on these 16 compounds (see Figure 6 for 13 selected parent PAH analysed in this PhD-thesis and Table 3 for some physico-chemical properties). These PAH encompass a wide range of properties. In general, fluoranthene and higher molecular weight PAH tend to bound to atmospheric particles while the lower molecular weight

PAH are preferably transported in the gas phase, due to the higher vapor pressure (Pankow 1987; Pankow and Bidleman, 1992)). Further on, lighter PAH are more vulnerable to direct or indirect photo-degradation by OH radicals, as a consequence of their free movement in the gas phase, than the particle bounded PAH that are protected by the particles (Brubaker and Hites, 1998).

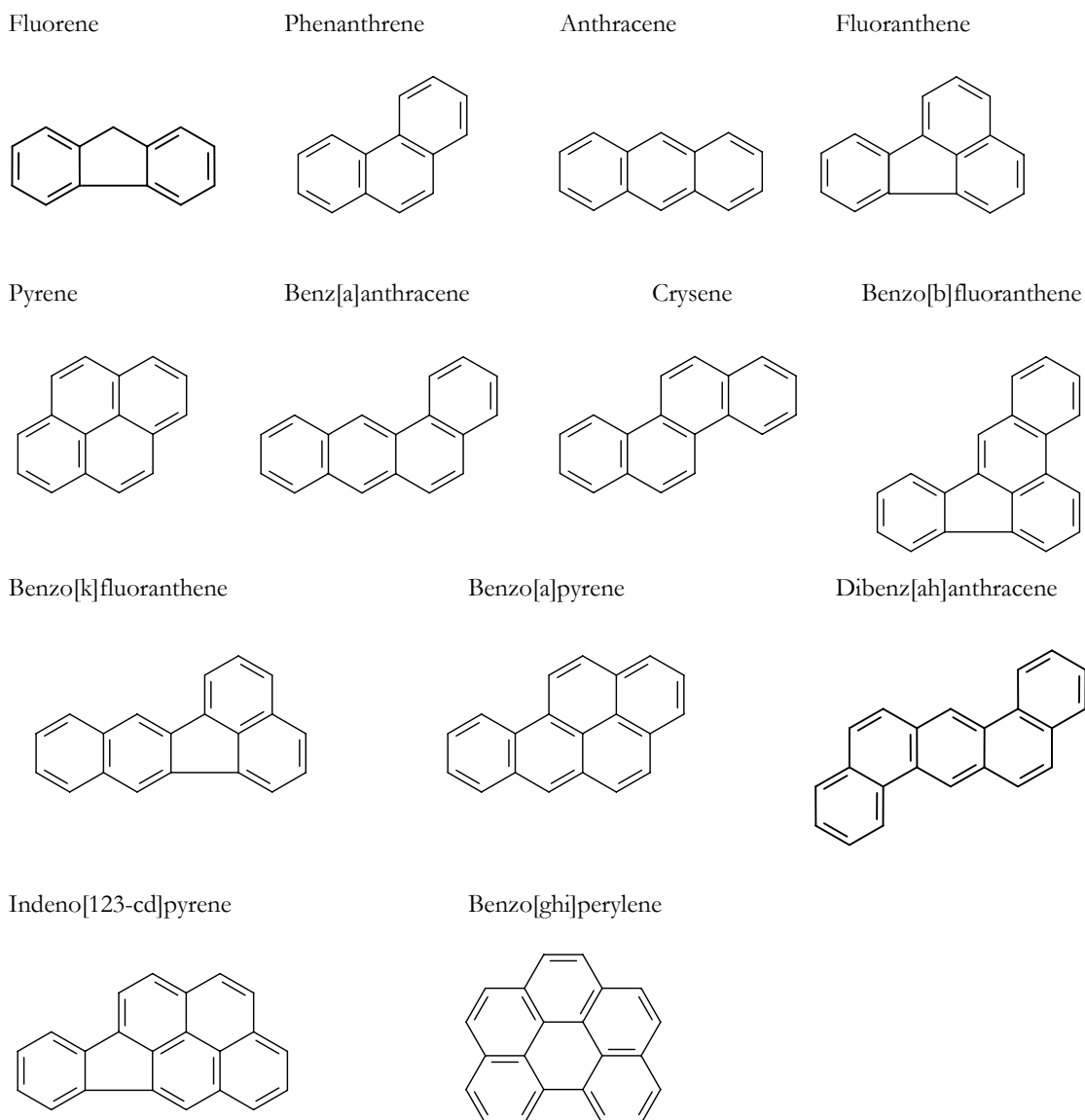


Figure 6. Molecular structures of studied PAHs

The particles that are directly related to the emission of pyrolytic PAH are black-carbon (BC). BC is produced by incomplete combustion of fossil fuels and vegetation fires. Like PAH it occurs ubiquitously. It can account for about half of the total organic carbon in certain soils. Structurally, BC may be essentially differentiated between soot-carbon (small particle size; SC) and char/charcoal. The former originate during the condensation of hot combustion gases involving free radical reactions of acetylene species leading into PAH, macro PAH, and SC. Conversely,

charcoal originates from incomplete combustion of plant tissue and diagenesis (Gustafsson et al, 2001) and always contains a core of unburned biomass material (with cell structure frequently discernible). During the past few years, the study of SC as a strong sorption matrix has received increasing attention (Bucheli and Gustafsson, 2000; Dachs and Eisele, 2000; Gustafsson et al., 2001). Adsorption onto SC has been shown to affect significantly the overall PAH sorption to sediments and aerosols. Since there seems to be a direct relationship between PAH and soot-carbon it is of interest to study the importance of this relationship in remote areas in order to understand the transport and world wide distribution of these pollutants.

Table 3 Selected physico-chemical properties of studied POPs at 278 K (Cotham and Bidleman, 1989); Ballschmiter and Wittlinger, 1991; Fischer et al., 1991; Guerin and Kennedy, 1992; Mackay et al., 1992; ten Hulscher et al., 1992; Dunnivant et al., 1992; Hargrave et al, 1997)

POP	Mol Wt. <sup>a</sup>	P <sub>L</sub> <sup>b</sup>	Log K <sub>ow</sub> <sup>c</sup>	H <sup>e</sup>
Fluorene	166	0.72	4.2	7.9
Phenanthrene	178	0.11	4.6	3.2
Anthracene	178	7.8 x 10 <sup>-2</sup>	4.5	4.0
Fluoranthene	202	8.7 x 10 <sup>-3</sup>	5.2	0.6
Pyrene	202	1.2 x 10 <sup>-2</sup>	5.2	0.9
Benz[a]anthracene	228	6.1 x 10 <sup>-4</sup>	5.9	0.6
Chrysene	228	1.1 x 10 <sup>-4</sup>	5.9	0.2
Benzo[b]fluoranthene	252		5.8	0.15
Benzo[k]fluoranthene	252	4.1 x 10 <sup>-6</sup>	6.0	0.11
Benzo[a]pyrene	252	2.1 x 10 <sup>-5</sup>	6.0	0.045
Indeno[123-cd]pyrene	276			
Dibenz[ah]anthracene	278	9.2 x 10 <sup>-8</sup>	6.8	0.069
Benzo[ghi]perylene	276	1.4 x 10 <sup>-8</sup>	6.5	0.076
HCB	285	3.1 x 10 <sup>-3</sup>	5.5	53
Alpha-HCH	181	7.3 x 10 <sup>-3</sup>	3.9	0.10
Gamma-HCH	181	1.9 x 10 <sup>-3</sup>	3.9	0.061
Alpha-endosulphane		6.2 x 10 <sup>-3</sup>	3.6	1.07
Beta-endosulphane		3.2 x 10 <sup>-3</sup>	3.6	0.04
4,4'-DDT	165	3.8 x 10 <sup>-5</sup>	6.0	6
4,4'-DDE	235	8.6 x 10 <sup>-4</sup>	5.7	34
PCB18	257	8.0 x 10 <sup>-2</sup>	5.6	32
PCB28	257	2.0 x 10 <sup>-2</sup>	5.8	29
PCB52	292	1.0 x 10 <sup>-2</sup>	6.1	32
PCB70	292	6.0 x 10 <sup>-3</sup>	6.3	17
PCB101	326	3.0 x 10 <sup>-3</sup>	6.4	25
PCB110	326	2.0 x 10 <sup>-3</sup>	6.3	20
PCB138	361	5.0 x 10 <sup>-4</sup>	7.0	13
PCB153	361	2.0 x 10 <sup>-4</sup>	6.9	17
PCB180	395	1.0 x 10 <sup>-5</sup>	6.9	11
PCB194	430	1.0 x 10 <sup>-5</sup>	7.6	29

<sup>a</sup> - molecule weight (a.m.u.);

<sup>b</sup> - sub-cooled liquid vapor pressure (Pa);

<sup>c</sup> - natural logarithm of the octanol - water partition coefficient;

<sup>d</sup> - Henry's Law Constants (Pa m<sup>3</sup> mol<sup>-1</sup>),



## **Chapter 3      Sampling sites in high-mountain areas**

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**Chapter 3      Sampling sites in high-mountain areas**

In the past and even nowadays high-mountain environments were regarded in awe by men. Hostile meteorological conditions, thin air, lack of vegetation, and difficult access made them considered to be homes of Gods and mythological spirits, as did belief the ancient Greek with Mount Olympus, the Norwegians with Jotumheimen ('Home of Ice Giants'), and the Tibetans with Chomo Longmu (Mount Everest) ('Mother of Mountains'), etceteras. At least they were no safe place for men, who limited their settlements to the valleys at lower altitudes. Scientific interest in mountain systems did not begin until mid-nineteenth century, although the first measurements of meteorological changes with altitude came much earlier. In September 1648 the effect of altitude on pressure was proved by Florin Périer, who operated a simple Torricelian mercury tube at the summit and base of Puy de Dôme, France, on request of his brother-in-law Blaise Pascal. And the French engineer H.B. de Saussure made observations of relative humidity during an ascend of Mont Blanc in August 1787. A year later he made developments on the temperature lapse rates in this area. After 1850 meteorological, geological and biological measurements began to be made systematically. It is in this period when different meteorological stations are established in European mountain regions. Through the years more stations were built in remote mountain areas all over the world. Besides the standard meteorological data, e.g. temperature, pressure, wind speed and precipitation, most of these stations are equipped nowadays with instruments for the analysis of solar radiation, aerosols, trace gases, like CO<sub>2</sub>, and POP. This is, for example, the case for the high altitude observatories of Izaña (2367m; Tenerife) and Mauna Loa (3399m; Hawaii). One of the latest features on atmospheric observations is the installation since 1989 of the high altitude Pyramid Laboratory in the Khumbu Valley of the Himalayas at an altitude of 5050m (Barry, 1992; Baudo et al., 1998).

Besides areas of scientific interest, nowadays the mountain regions nowadays are the majestic scenery for recreation and wilderness resources. In the recent years a number of international organisations, like the United Nations (UN) and the Inter-governmental Panel in Climate Change (IPCC), are devoting increasing attention to mountain issues, in order to protect and conserve these vulnerable areas. A specific point was also included in the Plan for Action into the 21<sup>st</sup> Century (Agenda 21 – Chapter 13) giving to mountain regions a priority in the global environmental-development agenda equal to that of other global change topics, such as climate change, desertification, or deforestation. Mountain regions have continued to move up in political and scientific agendas, and the UN dedicated 2002 as the International Year of the Mountains. Mountains are important. They contain unique vegetation and wildlife. They provide major freshwater deposits for water consumption and hydroelectric power generation. They often contain large forest reserves and sometimes contain valuable mineral resources. All together they cover around 20% of the earth's land surface, but little is known about the state of contamination. Nevertheless, recent international environmental research projects, like the European Community

financed projects AL:PE (*Acidification of Mountain Lakes: Paleolimnology and Ecology*), MOLAR (*Mountain Lakes Research*), and EMERGE (*European Mountain Lake Ecosystems: Regionalisation, Diagnostics and Socio-economic Evaluation*) have shown that the mountain systems may be remote but they are not at all pristine. They suffer from input of toxic chemical compounds, which could cause adverse effects on these fragile ecosystems.

The studied mountain areas in this PhD-thesis are separated into high-mountain ranges situated in the subtropical troposphere (e.g., the Island of Tenerife with the mountain of Teide) and the European continent (e.g., the Central Pyrenees and the High Tatras) (Figure 7). The separation of the areas is based on their different geographical situations and, as a consequence, different climatological conditions.

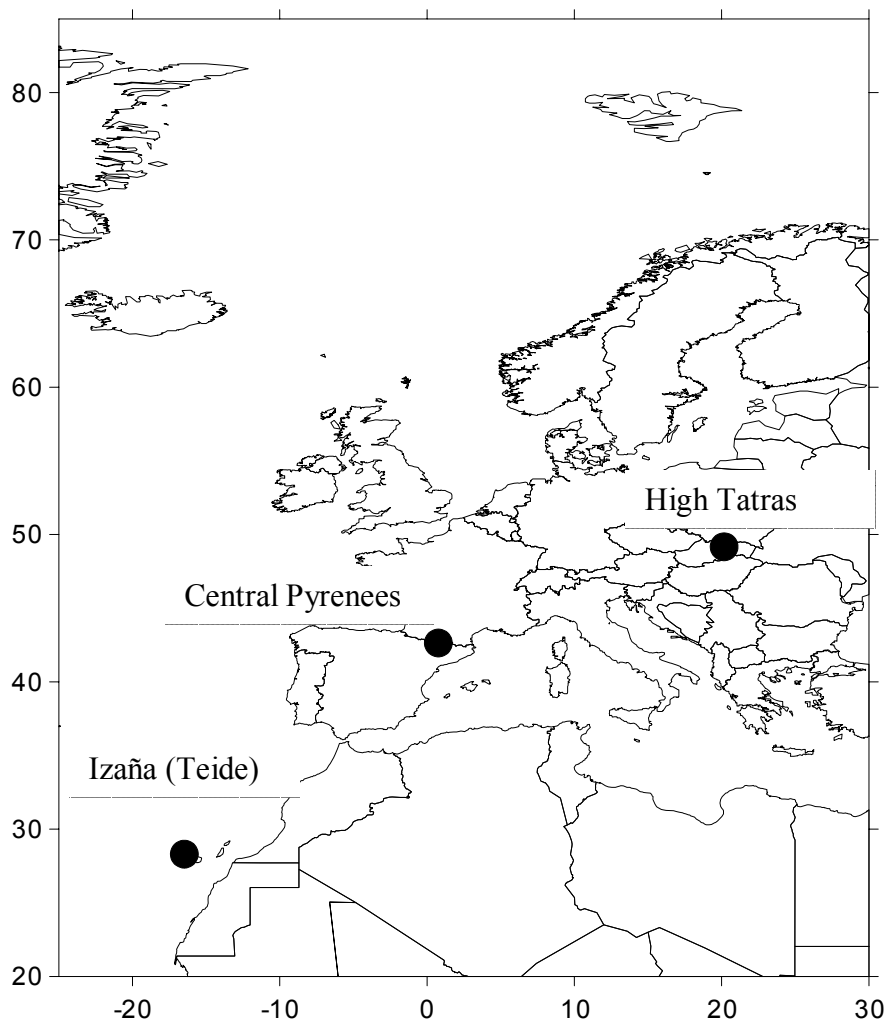


Figure 7. Geographical situation of the three studied high-mountain regions

### 3.1 Subtropical troposphere

#### 3.1.1 The Island of Tenerife

The Island of Tenerife ( $28^{\circ}18'N$ ,  $16^{\circ}29'W$ ) is the largest island (2057 km<sup>2</sup>) in the Canary archipelago. The distance from Tenerife to the African and European continent encompass ca. 350 km and 1300 km, respectively. The Canary Islands form, together with the Azores, Madeira and the Cap Verde, a triangle in the subtropical zone of the Atlantic Ocean called Macaronesia. All these islands have a volcanic origin (Castellano-Gil and Marcías, 1993). The highest volcano can be found in Tenerife, Teide (the place "where hell is vomiting fire").

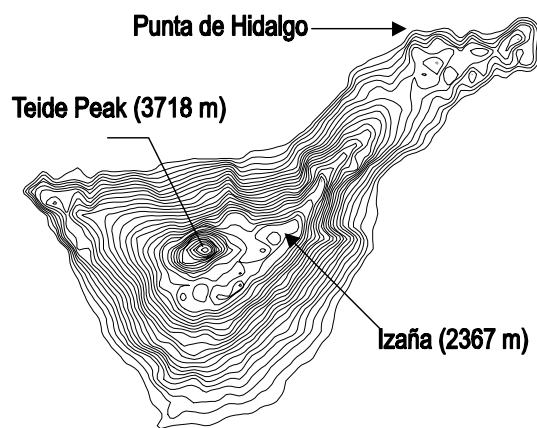


Figure 8. Island of Tenerife and atmospheric sampling sites.

The volcano of Teide, which rises up until 3718 masl, dominates Tenerife. In fact, the large environmental differences between the northern part of the island and the southern part are caused by its presence. The south side is arid, the north side is humid and green. Atmospheric samples were collected at the Atmospheric Observatory of Izaña (2367m) near the peak of Teide and at the lighthouse of Punta Hidalgo (40m) on the north-eastern side of the island (Figure 8). Soil samples were collected both on the northern and the southern slopes from sea level up to 3400m.

#### 3.1.2 Soils and vegetation

The soils of the Island of Tenerife are derived from volcanic ashes. In general they can be classified in three groups: sandy entisols in the Northern coastal area up until 600m, the inceptisols in the middle of the island, between heights of 800 and 1800m, and the pumice stone entisols above the local tree line (>2000m) (Fernández et al., 1982).

The island of Tenerife has many different ecosystems, which contain many endemic species, depending on its specific climate and relief. These conditions involve coastal ecosystems, where vegetation is under constant stress of strong winds and salt. These are the habitats of plant



species like 'lechuga marina' (*Astydamia latifolia*), 'salado' (*Schizogyne sericea*), 'balancón' (*Traganum moquinii*) and 'uvas de mar' (*Zygophyllum fonanesii*). In the higher areas of the coastal zone 'aulaga' (*Launaea arborescens*) can be found. In the humid places of the southern part of the island, on the basalt layer there are the endemic species 'cardones' (*Euphorbia canariensis*) and 'tabaibas' (*Euphorbia sp.*). Relief and climate also create ecosystems like the one of the north-eastern part, Anaga Mountains, called after a Guanche queen. It contains cloud forests that can be considered as living fossils of the forests that before the quartenaire era of glaciers covered vast parts of Europe. Typical laurel species are the Canary laurel tree (*Laurus indica*), the 'til' (*Ocotea forens*), the 'viñatigo' (*Persea indica*) and the 'barbuzano' (*Apollonia canariensis*). In the places where the forest was burnt down, or cut, another type of vegetation has developed, called Fayal-Brezal, characterised by the 'faya' (*Myrica faya*) and the 'brezo' (*Erica arborea*). Going up, from La Laguna to El Teide, one will pass the pinewoods, which are almost exclusively formed by the endemic Canary pine trees (*Pinus canariensis*). This species is adapted to the dry climate and is able to sprout after fires, or even recover itself after the fires. Above 1900 masl the landscape is occupied by bushes like 'laburnum' (*Adenocarpus foliolosus*) and 'retama blanca' (*Retama reatam*) (Castellano-Gil and Macías, 1993).

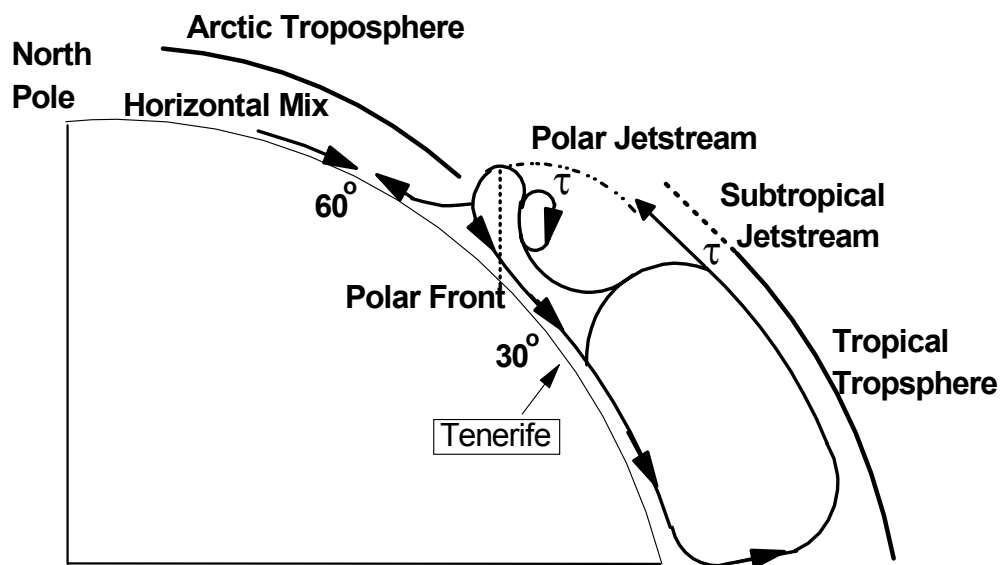


Figure 9. Hypothetical version of the heat/air mass circulation cells (adapted from Cuevas (1995))

### 3.1.3 Meteorological conditions

The local climate of Tenerife, and its different ecosystems, results from large-scale climatic phenomena, such as the circulation of heat/air from the equator to the poles. At the latitude of Tenerife (28°N) the circulation of the Hadley cell dominates the meteorology as explained below. This cell is located between the equator and both sides of the hemispheres up to 30°N and S (Figure 9). Due to the unequal irradiation, absorption, and reflection of sunlight on the world surface, there is a net gain of heat between 20°N and S and a net loss of heat at the higher latitudes. These differences have to be compensated by a transfer of heat from the equatorial zones to the

higher latitudes by ocean currents. In addition the evaporation of water plays a smaller, but important role in the transport of heat on a global scale (Wells, 1997). The evaporation of water in the tropics causes rain fall and strong low air pressure bands in the lower atmosphere along the equatorial zone, mostly in the Inter-tropical Convergence Zone (ITCZ). These are the zones where the great tropical rainforests are situated. At latitudes of 30°N and S the ascended air from the tropics descends, causing relatively warm (high potential temperature) and dry air at these latitudes. Here, high-pressure areas, or anticyclones, are common and these are the zones of the largest deserts in the world (Cuevas, 1995; Open University, 1989). Ascending air masses along the equatorial zone and the descending air masses along the subtropics causes a pressure gradient between the subtropics (high) and the equator (low). Because of Earth rotation (causing the Coriolis force) and the friction of air at the surface, this air flow does not go straight in north-south direction, but in a general NE-direction in the northern hemisphere and a SE-direction in the southern hemisphere (Wells, 1997; Open University, 1989). In the days that Europeans (like Columbus) rediscovered the new worlds and the colonial trade started off, sailing vessels used these constant winds. In the English language this defined them operationally: trade winds.

These trade winds play a very important role in Tenerife. Because of the large and stable high pressure areas located around the Azores round the year (Azores high), wind comes from a dominated NE-direction. During their journey from the north-west coast of Africa and temperate zones in the direction of the ITCZ, the warm surface air from the continent is rapidly transformed by contact with the cooler surface water in a shallow marine boundary layer, or mixing layer. The moisture content of the mixing layer is rapidly increased by the water evaporation from the ocean, whilst sensible heat is lost from the air to the ocean because of the reversal of the temperature gradient (Wells, 1997). At the latitude of Tenerife the mixed layer has reached a thickness of around 1500m, and the surface air has more or less the same temperature as the sea surface, around 18°C. Because of the addition of water vapour and the net cooling low stratus clouds are formed in the mixed layer. The atmospheric sampling site at Izaña (2367m) is situated above this layer, while Punta de Hidalgo (40m) is situated within. In the north side of the island a field of stratus clouds can form especially during daytime, which is visible from above the mixed layer and is called 'Mar de Nubes' (Sea of Clouds). This cloud field has its maximum frequency and extension in summer, when the evaporation of the seawater is highest and the trade winds are more intensive. The suppression of the marine boundary layer is further enforced by a strong temperature and humidity inversion. Above the marine boundary layer, the air has a high potential temperature and is very dry, representing the Free Troposphere. In contrast, the air in the marine boundary layer has a relative low potential temperature and high humidity. The two air masses are completely different (Font Tullot, 1956, Castellano-Gil and Macías, 1993, Cuevas., 1995, Wells, 1997). The trade wind inversion shows annual variation. Annual shifting of the subtropical highs causes annual variation in intensity of the trade wind inversion and altitude of the Sea of Clouds. In summer the inversion

is more intensive than in winter and the zone of the subtropical highs is situated at higher latitudes ( $45^{\circ}$  N) causing an increase of relative humidity because of stronger and longer trade wind influences. Also soil warming during summer causes an extremely dry air mass above the boundary layer and forces the inversion between the two air masses. In winter the zone of the subtropical highs is situated at the latitude of Tenerife ( $27,5^{\circ}$ N) (Cuevas, 1995), and the trade wind inversion is broken up frequently, because of the decreasing differences between the air masses. In these cases trade wind air can mix with the air of the Free Troposphere.

In the Free Troposphere, above the inversion layer, the influence of the Coriolis force and friction with the earth surface is small. At Izaña (2367m) the wind is coming predominantly from a NW-direction. In the summer months an anticyclone is frequently formed above north Africa and the island is situated between two high pressure areas (Font Tullot, 1956). This situation causes frequent invasions of dust from the Sahara in these months. However, in winter the sub-tropical jet stream (very strong westerly wind between the tropical and the moderate latitudinal tropopause) is located above Tenerife causing a very strong and cold NW wind, with air that has its origin in the sub-polar zone. The annual wet deposition over the period 1961-1989 at Izaña is around 500mm, with 69% of the precipitation from November until February.

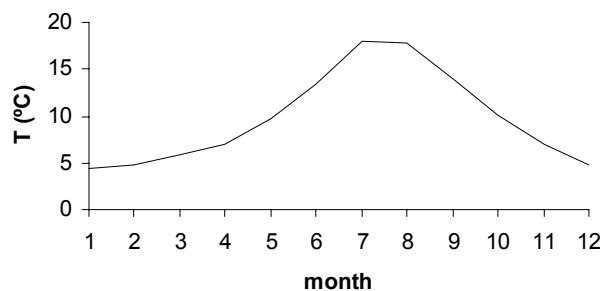


Figure 10. Average atmospheric temperature at Izaña (2367m) for the period between 1961 and 1989 (adapted from Cuevas (1995)).

In the period November - February the Sea of Clouds can reach the height of the observatory and causes precipitation in the form of rain or snow. The mountain can be completely covered with snow. In summer, however, it is extremely dry. Although the sky is covered 76 days of the year (mainly occurring in wintertime), Izaña has many sun hours (77% of its time). The average monthly temperatures at Izaña are shown in Figure 10.

### 3.1.4 Human activity

Since the 18<sup>th</sup> century travellers, scientists, naturalists and foreign businessmen have established themselves on the island. At the end of the 19<sup>th</sup> century the exportation of tourism became an interesting economic alternative. Hotels were built and several societies were established.

Due to different problems, e.g. world wars and economic depressions, tourism did not develop to its actual extent until the 1960s. This activity became a cultural phenomenon that greatly influenced the Canarian economy and environment.

In the 21<sup>st</sup> century Tenerife became a modern island whose economy was dominated by agriculture (especially wine and banana), trade, tourism and small-scale industries form the principal economy. Although, the island is quite populated there is practically no habitation above 1000m. People are concentrated along the coast. The most important industrial activities are a petrol refinery and a power plant located north-east and east of the Izaña Atmospheric Observatory, respectively. However, at both atmospheric sampling sites (lighthouse of Punta de Hidalgo and Izaña) and the soil sampling sites, the influence of the human activities can be neglected (Castellano-Gil and Macías, 1993; Cuevas, 1995).

### 3.2 European high-mountain areas

The two areas studied here, the Central Pyrenees and the High Tatras, are very similar in many aspects, such as geological formation, geomorphology of the lake basins and general climatological conditions. Both areas are part of larger mountain ranges, forming an important part of the orography of the European continent. Due to their extension, their complex orography, and their situation in the continent, they have major influences on regional and local climates. Moreover, they are located on temperate latitudes.

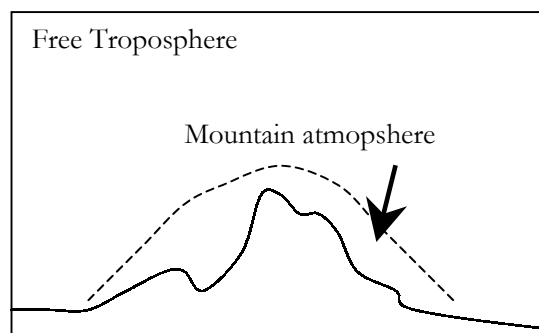


Figure 11. The mountain atmosphere. Adapted from Barry (1992).

In contrast to Conversely of the 'simple' meteorological conditions of Tenerife, which rises up as a needle in the middle of the subtropical Atlantic Ocean, the atmospheric situation in the European high-mountains is much more complex. In these sites the atmosphere is not representative of the Free Troposphere, as in Tenerife, but of a Mountain Atmosphere (Barry, 1992) (Figure 11). Inversion or boundary layers are less defined as they were on Tenerife. In Europe, the Westerlies play an important role on the weather and wind patterns. These systems are associated with depressions or frontal cyclones from the Atlantic Ocean cause abundant precipitation in the north/western part of the European continent. In the continent, air masses find

obstacles like the mountain ranges, which generates an ascent. Descending air pressures with altitude result in descending air temperatures causing saturation of the water content of the air masses, and consequently altered precipitation. Depending on arrival of cold or warm fronts to the mountain ranges the precipitation can be more or less abundant. Furthermore, influence of low altitude air masses at higher sites depends on the type of front (Barry, 1992). These phenomena may cause smaller scale effects, like higher precipitation at higher altitudes, or at the slopes where the frontal cyclones find the mountain ranges, while on the other site of the mountain range dry air is descending. Furthermore, slopes may be heated up during daytime causing small scale low pressure zones, which result in air flows from lower parts of the valley to the mountain (valley-mountain breeze). Conversely, descending air temperatures at higher altitudes in the night-time may provoke a descending airflow from higher sites towards the valley (mountain-valley breeze). Stable atmospheric situations (high atmospheric pressure) often results in a temperature inversion, where cold (and often humid) air occupies the valley, while mountaintops are bathing in the sun. A sea of clouds is often visible in these cases, which is more persistent in wintertime (Barry, 1992).

The sites for atmospheric, soil and sediment sampling were all far away from potential local contamination sources. Thus, they can be considered as sites under the influence of long-range transport of contaminants. Nevertheless, regional scale meteorological conditions may affect their air quality.

### **3.2.1 Central Pyrenees: Estany Redon**

The Pyrenees are situated in the connection of the Iberian Peninsula and the rest of the European continent and range from the Mediterranean Sea to the Atlantic Ocean over a length of about 435 km. Estany Redon is located in the Central Pyrenees, where the mountains reach their maximum height up to 3404m (Pic d'Aneto). The mountain range was formed around 50 Million years ago, when the Iberian landmass collapsed into the European continent. In the same period other alpine areas, like the High Tatras, the Alps and the Himalayas, were formed.

#### **3.2.1.1 Geographical situation and origin of Estany Redon**

Estany Redon (42°03'33,5''N; 0°46'12,7''E; 2240m) is an oligotrophic high mountain lake located in the Catalan part the Central Pyrenees. There is some confusion in the literature about the name of the lake. Redon is its correct name as it is in Occitane, the official language of Vall d'Aran, the county in Catalonia where Occitane and not Catalan is spoken. Sometimes it appears in the literature as Llac Redó or Redo, which corresponds to its Catalan name. In all cases, Estany Redon means 'round lake'. It is situated at the higher end of the valley of Noguera Ribagorçana, and forms one of the headwaters of the river with the same name. The lake is accessible by the two-lane

highway N-230 until the tunnel of Vielha, where the High Mountain Research Centre (CRAM; 1600m) is located. From this site the lake is reached by walking up in eastern and northern direction through the valley of Conangles and the Barranc del Redó, respectively, passing a forest of beech (*Fagus sylvatica*), silver fir (*Abies alba*), *Pinus uncinata* and finally high mountain pasture.

The basin of the lake is open in the southern direction and surrounded in the west by the Tuc de Port deth Vielha (2606m), in the east by Tuc de Sarraera (2632m) and Tuc de l'Estany Redon (2540m), and in the north by the ridge between the two highest summits. This range forms the divisor between the southern and northern slopes of the axial of the Pyrenees. The outflow of the lake, in southern direction, flows into the Barranc del Redó and the valley of Conangles to the Noguera Ribagorçana river. In this direction the altitude loses 600m in less than one kilometre.

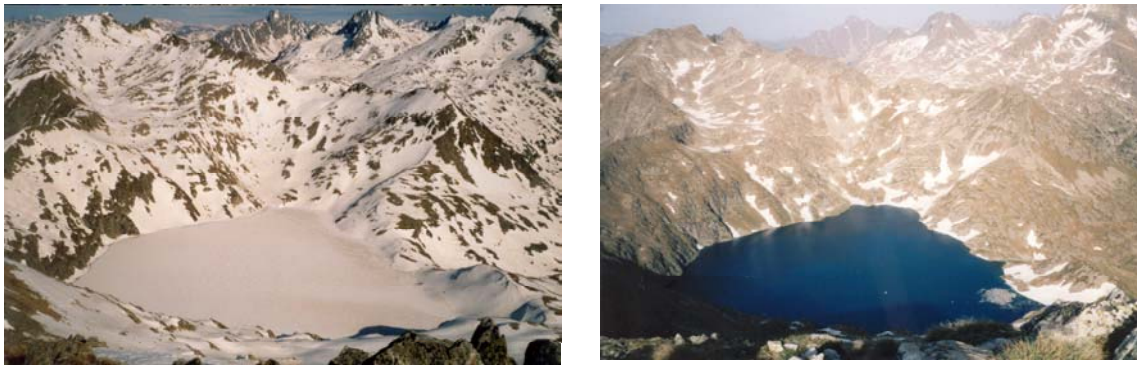


Figure 12. Estany Redon in March and June 2002. Photos are taken from Tuc deth Port de Vielha in eastern direction.

The lake is formed by the activity of glaciers in the Pleistocene coming down from the Tuc deth Port de Vielha in eastern direction and from the Tuc de Sarraera in western direction. While in the north of the Northern Hemisphere whole landmasses were ice covered, in the southern parts only the mountain chains were ice covered. The lake is a glacial cirque that was feeding the glaciers that went down through the Vall de Conangles in the direction of the valley of Noguera Ribagorçana. The work of the glaciers in the past and the present climatic conditions result in a lake with a depth of around 70m and a surface of around 24 Hm<sup>2</sup>. This makes Estany Redon one of the high mountain lakes in the Pyrenees with the largest volume (7.75 hm<sup>3</sup>) (Catalan 1987; 1988).

### 3.2.1.2 Geomorphology, soils and vegetation

The amphitheatre-like shape of the basin is all granite (granodiorita of the Maladeta) corresponding to the late-hercinian intrusion. The whole catchment of the basin is 155Hm<sup>2</sup> from which 16% is occupied by the lake surface. Due to the activity of the ice, a threshold of rock blocks was formed in the southern part (the exit of the glacier). The whole basin shows a degraded image due to the intense dynamics of the ice. The lake does not have a principal entrance of water, but

multitude sources in the rocky catchment, most water is incorporated from direct atmospheric inputs. This explains the oligotrophic character of the lake. Further on its waters have low ion levels, which are just high enough to sustain the brown trout (*Salmo trutta*) community living in this lake (Table 4). In dry periods the lake does not receive water (Catalan 1987; 1988).

Three dominant types of land cover are found in the lake catchment; dry alpine meadows, moraines, and solid rock. Due to the steep slopes, the rock types and the cold climatic conditions the soils in the dry alpine meadows are poor developed (leptosol, histosol, and podsol) with a black acid humus layer and a mineral (sand) horizon of few centimetres thickness directly covering the bedrock. Lichen and mosses cover a considerable part of the rocky basin. Due to the geographical position and the altitude the basin contains alpine vegetation. The predominant species are *Festuca eskia* and *Carex sempervirens*, which are situated on the sun spotted sites and steep slopes. Further on, some individuals of *Rhododendro* and *Pinus uncinata* are growing sparsely and in bonsai form (Catalan 1987; 1988).

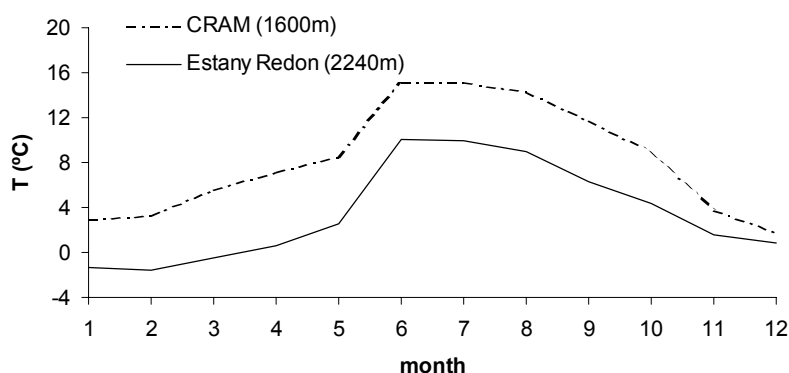


Figure 13. Average monthly atmospheric temperatures in 2002 at CRAM (1600m) and Estany Redon (2240m)

### 3.2.1.3 Meteorological conditions

The alpine climate of the valley and near the lake consists of cold winters and relatively cool summers. Figure 13 shows the average monthly temperatures at CRAM (1600m) and Estany Redon (2240m). The average annual temperature at Estany Redon is about 3.2°C, while this temperature is around 8.8°C at altitude of CRAM (1600m). The lake starts to freeze up normally around the beginning of December and stays ice and snow covered until late May (Figure 12). The yearly wet precipitation at Estany Redon is around 1500mm. In winter it is essentially constituted of snow. During the rest of the year precipitation is in the form of rain, but it is of less importance at this altitude (Catalan 1987; 1988). The air masses arriving to the sample site may have their origin on the European continent as well as the Atlantic Ocean. Now and then the site receives dust invasion from the Sahara (Camarero and Catalan, 1996).

#### 3.2.1.4 Human activity

Besides the researchers visiting the lake basin, it is also visited now and then by excursionists. In some cases illegal trout fishing takes place. The lake is situated in a natural environment with human small scale human activities in the valleys. The valley of Noguera Ribagorçana, 600m below the lake in the south, contains few small villages. Senet at  $\pm 9$ km distance is the nearest by. Here there are no industrial activities. A two-lane highway N-230 is passing through the valley ending in a tunnel. On the other side of the mountain range, in the north, where the tunnel is ending, Vall d'Aran is located. None of its villages has important industrial activities and no OC contamination is expected to arrive from these sites. In case of the PAH, combustion of wood in household fires and eventually forest fires are the two main possible sources. Further on, the incendiary of Vielha, located on the northern exit of the tunnel of Vielha (Vall d'Aran), could play a role in the PAH levels and composition, together with the traffic on the highway N-230 itself of course. However, besides these regional sources of small intensification and scale, the effect of the human activity concerning POP is considered to be low.

### 3.2.2 The High Tatras

These mountains are situated on the national borders of the Slovakian Republic and Poland ( $20^{\circ}0'E$ ,  $49^{\circ}4'N$ ). The length is about 34km from east to west and the wide is about 10km, which makes it the smallest alpine area in Europe, with modest heights up until 2654m (Gerlachovský štít) and 2634m (Lomnický štít). The High Tatras, or Vysoké Tatry, form the highest part of the Carpathian range. The area is not only a National Park since 1949, it also has become a Biosphere Reserve under the UNESCO Man-and-Biosphere-program since 1993. Therefore, it receives special environmental protection.

#### 3.2.2.1 Geographical situation and origin of the studied lakes

All studied lakes are situated above the local tree line, where glaciers in the past have formed amphitheatre-shape basins. The formation of the lakes as a consequence of the glacier activity is similar to that of Estany Redon. After the retreat of the glaciers about 10.000 yr. ago more than 100 lakes had been formed in the High Tatras. The soils and sediments of the oligotrophic lakes studied in this PhD-thesis are Długi Staw ( $49^{\circ}13'36''N$ ;  $20^{\circ}00'39''E$ ; 1783m), Starolesnianske Pleso ( $49^{\circ}10'48''N$ ;  $20^{\circ}10'04''E$ ; 2000m) and Ladové Pleso ( $49^{\circ}11'03''N$ ;  $20^{\circ}09'46''E$ ; 2057m) (Table 4). The first lake is situated in the north-western (Polish) part of the High Tatras in the Gasienicowa Valley, which is open to the north-east. The last two lakes are situated on the south-eastern part of the range, in the Velká Studená Valley, which is open in the south (Figure 14). The atmospheric samples were collected at the meteorological observatory of



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Skalnaté Pleso (49°06′36″N; 20°08′24″E; 1778m) of the Slovakian Meteorological Service (SAV), which is situated close to the later Velká Studená Valley.

Figure 14. Ladove Pleso and Starolesnianske Pleso in the valley Velká Studená Valley (Foto: Ladislav Jiroušek).

### 3.2.2.2 Geomorphology, soils and vegetation

The bedrock in all studied sites is granite. Three dominant types of land cover are found in the catchment: dry alpine meadows, moraines, and solid rock. Due to the steep slopes of the surrounding mountain peaks, rock types and cold climatic conditions, the soils in the dry alpine meadows are undeveloped (leptosol, histosol, and podsol) with a shallow organic horizon (0.05 – 0.17m; 0.14m) and 0.33m deep mineral horizon.

The vegetation in the High Tatras is marked by its great diversity in both horizontal and vertical gradients. Beech (*Fagus sylvatica*), fir (*Abies alba*) and Norwegian spruce (*Picea abies*) dominate the (lower) mountain (sub)-montane zone (up to 1250m). The upper mountain (supremontane) zone (up to 1550m) is almost completely covered by Norwegian spruce, European larch (*Larix decidous*), and arolla pine (*Pinus cembra*). The subalpine zone (up to 1800m) is covered with dwarf pines (*Pinus mugo*). This small pine tree species forms the tree line. The alpine zone is occupied by alpine tundra, formed by *Salix reticulata*, *Salix herbacea*. The vascular plants are getting scarce with altitude and the rocks are covered with lichens and mosses, of which the snow andreaea moss (*Andreaea nivalis*) is typical.

### 3.2.2.3 Meteorological conditions

The climate of the High Tatras is determined by their situation in the heart of central Europe and is characterised by a high degree of continentality. There are large differences between summer and winter temperatures and there is high precipitation in summer. The annual

atmospheric temperature at the summits is  $-3.8^{\circ}\text{C}$ . At the atmospheric sampling site of Skalnaté Pleso (1778m) the average annual temperature is  $1.6^{\circ}\text{C}$ . Figure 15 shows the average monthly temperature over the period between 1930 and 1960 for Skalnaté Pleso (178m). The average temperatures in the warmest month, July; at 1018m, 1778m and 2634m are  $14.4^{\circ}\text{C}$ ,  $10.0^{\circ}\text{C}$  and  $4.2^{\circ}\text{C}$ , respectively. The temperature inversions are frequent in the air layers of valleys and basins. The mean annual precipitation increases with altitude from 650mm to 1350mm and 2200mm, at 1018m, 1778m and 2634m, respectively. The days of precipitation also increase with altitude being 190 days (90 days snowfall) at 1018m and 215 days (150 days snowfall) at 2634m (Lomnický štít). Between the altitudes of 1018m and 2634m the areas are snow-covered between 130 and 240 days. The studied lakes are normally frozen from November until June.

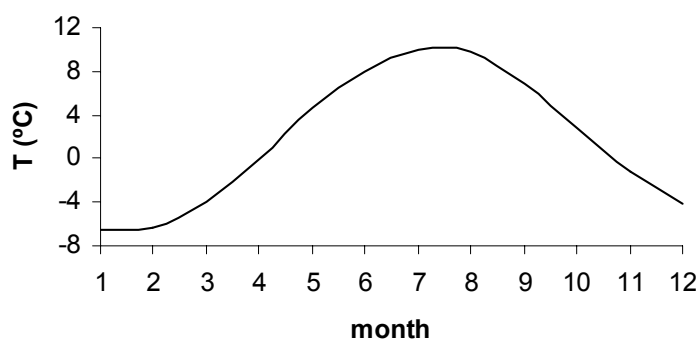


Figure 15. Average temperatures at Skalnaté Pleso (1778m) over the period 1930-1960 (adapted from Mikulaš Konček et al. (Konček, 1974))

#### 3.2.2.4 Human activity

Besides excursionism, alpinism, ski tourism and scientific research, there are no other important activities taking place in the High Tatras. Because of its status as National Park and Biosphere Reserve the High Tatras receive special and strict nature conservation regulations. It is therefore impossible to enter the area by car. There are only two places where the park is accessible by cable cabin. Even the huts situated in the park need to be supplied by manpower, so without use of donkeys or helicopter. This last feature has turned into a tradition among the mountaineers to carry as much load as possible on their backs up to the mountain. The record is held by the owner of the hut Skalnatá Chata, Laco Kulanga, who carried 207.5kg of supply 530m up to the mountain in less than 6 hours. At lower parts of the mountains some forest management is done. The Tatras are further surrounded by relatively small settlements. The largest nearby cities are Zakopane, in the north-west of the mountain range, and Poprad, in the south-east. Both cities are situated at distances of about 50km from the High Tatras. After the Second World War (WWII) the region has remained quite rural. However, in different parts of the former Eastern Germany, Czechoslovakia and Poland mining, metallurgical and chemical industry were highly developed. Contamination

effects of emissions from these industries are documented and reflected in the destruction of forests by acid rain and the acidification of the lakes from the Bohemian Forest and Sweden (Kopáček et al., 2002). The effect of atmospheric contamination in the High Tatras is measured in the waters and sediments of its lakes, where very high levels of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and PAH were found (Fernández et al. 1999; 2000; Kopáček et al., 2002).

Table 4. Physical characteristics and water chemistry of the studied lakes

Name		Estany Redon	Długi Staw	Starolesnianske Pleso	Ladove Pleso
Geo. Position		42°03'N; 00°46'E	49°13'N; 20°00'E	49°10'N; 20°10'E	49°11'N; 20°09'E
Altitude	(m)	2240	1783	2000	2057
Area catchment	(ha)	155	65	2	13
Area lake surface	(ha)	24	1,6	0,7	1,7
Max. depth	(m)	73	11	4	18
Alk.	(meq/L)	45	22	2	65
PH		6,7	6,2	5,3	6,6
TOC <sup>1</sup>	(mg/L)	1,1	0,2	4,2	na <sup>2</sup>
TP	(µg/L)	1,0	1,0	8,0	2,0
TN	(µg/L)	220	534	211	276
Cond.	(mS/m)	1,2	1,5	0,9	1,4

Data from EMERGE project 2000; 1) TOC data from MOLAR project; 2) na: not analysed.