



PERGAMON



Atmospheric Environment 35 (2001) 245–254

ATMOSPHERIC
ENVIRONMENT

www.elsevier.com/locate/atmosenv

Persistent organic pollutants in snow from European high mountain areas

Guillem Carrera, Pilar Fernández*, Rosa M. Vilanova, Joan O. Grimalt

Department of Environmental Chemistry Institute of Chemical and Environmental Research (CSIC), Jordi Girona, 18-26, 08034 Barcelona, Catalonia, Spain

Received 19 January 2000; received in revised form 13 March 2000; accepted 28 March 2000

Abstract

Snow cores were collected in the catchment area of five remote mountain lakes in Europe. They were analysed for polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), and organochlorine pesticides, namely DDTs, hexachlorobenzene (HCB) and hexachlorocyclohexanes (HCH). PAH are found in higher amounts in the Tatra and Caledonian mountains, PCB are higher in the Alps and HCH are highest in the Alps and Pyrenees. The qualitative PAH distributions are dominated by low molecular weight compounds, phenanthrene being the most abundant PAH in all but in one site. These compounds also occur predominantly in the gas phase in the atmosphere. Their high abundance in the snowpack witness the occurrence of effective transfer mechanisms from gas to snow flakes. In Starolesnianske (Tatra mountains), a higher contribution of high molecular weight compounds is found. This site exhibits the highest snow PAH and suspended particulate levels. Transformation of the concentration values of these compounds into annual deposition rates and correction for catchment/lake area indicates that in Scandinavia and the Alps a large proportion of PAH incorporation is mediated by snowfallout whereas in the Tatra mountains snow deposition only accounts for a small fraction of the compounds stored in the lake sediments. Among organochlorine compounds, only PCB and HCH have been found above method detection limit in most of the samples. The PCB congener distributions changes significantly between sites, although a predominance of the less chlorinated congeners have generally been observed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Snow; Deposition; PCB; PAH; HCH; Remote lakes

1. Introduction

Snow and ice influence the deposition and fate of persistent organic pollutants (POPs) in cold regions (Hoff et al., 1995). Due to their high porosity, falling snowflakes have been proposed to be more effective at scavenging atmospheric particles than rain (Franz and Eisenreich, 1998). In addition, the large specific surface area of ice crystals enhances the adsorption of gaseous hydrophobic contaminants from the atmosphere (Wania

et al., 1999). Hence, the concentrations of airborne contaminants in the snowpack represent an integration of the atmospheric deposition over certain period, and can be used for estimating pollutant levels in the region.

After deposition, the trapped semivolatile compounds undergo a number of processes, such as repartitioning and translocation within the snowpack, volatilisation and drainage at the time of snowmelt (Wania et al., 1998). Release of the accumulated substances into adjacent aquatic systems can represent a significant load of contaminants over a short period.

Most of the available literature regarding the occurrence of POPs in snow pertains to high-latitude areas (Franzén et al., 1994; Gregor and Gummer, 1989; Jaffrezou et al., 1994; Patton et al., 1989; Rahm et al., 1995;

*Corresponding author. Tel.: +34-93-4006100; fax: +34-93-2045904.

E-mail address: pfrqam@cid.csic.es (P. Fernández).

Risebrough et al., 1976; Tanabe et al., 1983; Welch et al., 1991). Few works have been published in relation to the accumulation at lower latitudes and those available correspond to North America (Blais et al., 1998; McConnell et al., 1998).

In a previous study, high levels of airborne contaminants have been detected in sediments from high-altitude European mountain lakes (Fernandez et al., 1999) despite their remoteness and absence of nearby human activities.

In order to gather information on the origin, transport processes and deposition pathways of these pollutants, POPs in snowpack have been studied in the catchment area of these remote lakes. Polycyclic aromatic hydrocarbons and organochlorine compounds, two main compound groups among POPs, have been examined. The results are compared with the previous sedimentary and atmospheric data available from these sites (Fernandez et al., 1996, 1999; Vilanova et al., 1998). Differences in qualitative distributions and concentrations are discussed in terms of origin and scavenging mechanisms. The results have been used to infer winter deposition patterns in each site.

2. Experimental

2.1. Sampling

Total snowpack was hand cored with a pre-rinsed stainless-steel corer at each sampling site (Table 1). In some cases specific snow layers were collected. Snow depth (in water equivalents) and snow density were determined. Snow samples were transferred to pre-rinsed stainless-steel containers and covered with aluminium foil. These containers were kept at room temperature in field laboratory facilities until complete thawing. Then, the organic pollutants were recovered from the water (1–2 l) as described in Carrera et al. (1998). The particulate matter was separated by filtration through pre-weighed glass fibre filters (Whatman, GF/B, 45 mm diameter, 1 µm pore size) and the dissolved fraction was recovered by adsorption on solid-phase extraction disks (C18 Empore disks, 47 mm diameter, 0.5 mm thickness). Both, filters and disks were wrapped in aluminium foil and frozen for transport and storage until analysis. Glass fibre filters were freeze-dried and total amount of particles in snow were determined by weight difference.

Table 1
Meteorological conditions and characteristics of the snow samples

Lake	Redó	Gossenkölle		Jöri III		Starole-snianske	Øvre Neådalsvatn	
Annual precipitation (mm)	1800	1300		1500		1200	1700	
Snow precipitation (%) ^a	50	54		65–70		28	n.a. ^b	
Abbreviation	RED	GKS-March	GKS-May	JOR-97	JOR-98	STAR	OVRE-97	OVRE-98
Sampling date	Feb-98	March-97	May-97	Feb-97	Feb-98	March-98	March-97	March-98
Sample type	Core	Core	Core	Layer	Core	Core	Layer	Core
Winter temperature (°C) ^c	– 0.5	– 3.6	– 3.6	– 5.2	– 5.3	– 1.9	n.a.	n.a.
Sample precipitation (mm) ^d	430	320	580	480	380	340	n.a.	n.a.
Water equivalents (cm)	38	38	64	33	33	45	—	88
Snow depth (cm)	130	n.a.	n.a.	0–15/ 50–70 ^e	150	60	n.a.	n.a.
Particles (mg/l)	1.1	1.0	0.82	0.24/ 1.3	3.5	2.0	1.0	2.3

^aPercent of annual precipitation in snow form.

^bn.a., not available.

^cMean temperature from October to April.

^dTotal precipitation corresponding to the period of snow accumulation represented by the core (from October to the sampling date of each core). Within the sampling period more than 95% of this precipitation was in snow form.

^eSamples corresponding to two snow layers of a core.

2.2. Extraction and analysis

Freeze-dried glass fibre filters were extracted by sonication with dichloromethane : methanol (2 : 1) (3 × 10 ml, 20 min each). The compounds adsorbed in membrane extraction disks were eluted with methanol (5 ml), cyclohexane (5 ml) and dichloromethane (5 ml) as described elsewhere (Carrera et al., 1998). The elutants were mixed and dried over anhydrous sodium sulphate. A recovery standard mixture of perdeuterated anthracene-d₁₀, pyrene-d₁₀, benzo[ghi]perylene-d₁₂, and PCB nos 30 and 209 was added to the filter and adsorption disk extracts. Then, they were vacuum-evaporated until almost dryness and fractionated with aluminium oxide as described in Fernandez et al. (1999). Organochlorine and aromatic compounds were eluted with dichloromethane : hexane (1 : 19) and dichloromethane : hexane (2 : 1), respectively. The fractions were vacuum-evaporated to 1 ml and transferred to vials by a gentle stream of nitrogen. Prior to instrumental analysis, samples were spiked with an internal standard mixture of tetrachloronaphthalene, octachloronaphthalene, perdeuterated naphthalene-d₈ and perylene-d₁₂ dissolved in isoctane.

2.3. Instrumental analysis

Quantitative analysis of aromatic and organochlorine compounds was carried out by gas chromatography coupled to mass spectrometry, operating in the selected-ion monitoring (SIM) and electron impact modes. The instrumental conditions are described in detail elsewhere (Fernandez et al., 1999).

Quantitation was determined by the internal standard method. Reported values were corrected for blanks and surrogate recovery. Method quantitation and detection limits (Table 2) were calculated for each snow sample, e.g. pp'-DDT detection limits in dissolved and particulate matter were 94 and 152 pg, respectively, and the respective quantitation limits were 157 and 254 pg. These thresholds correspond to signal-to-noise ratios of three and five, respectively. Pollutant levels were reported only when they exceeded the quantitation limits. For compounds not detected in any sample, detection and quantitation were assumed as those calculated from standard mixtures (Carrera et al., 1998).

Table 2
Concentration of persistent organic pollutants in snow. Results from other areas are included for comparison

Site	PCB ^a (ng/l)	HCH ^b (ng/l)	DDTs (pg/l)	PAH ^c (ng/l)	Reference
Jöri	2.2	0.49	BDL ^d	16	This study
Gossenkölle	0.73	1.1	330	17	This study
Redó	0.22	0.52	BDL	5.6	This study
Starolesnianske	0.20	0.022	73	81	This study
Ovre Neadalsvatn	0.73	BQL ^e	BDL	25–32	This study
Arctic (Canada)	0.02–1.8 ^f	0.74–13	50–70		Gregor and Gummer, 1989
Arctic (Canada)		0.67–2.6			Patton et al. (1989)
Arctic (Russia)	5.3	5.6	2100		AMAP (1998)
Canadian Rocky Mountains	~ 1.1–1.4	0.17–0.43			Blais et al. (1998)
Lake Siskiwit (USA)	1.5 ^g				Swackhamer et al. (1988)
				85 ^h	Mc Veety and Hites (1988)
Antarctica	0.16–1.0	2.3–4.9	15–17		Tanabe et al. (1983)
Doumer Island (Antarctica)	0.03–0.3		490–630		Risebrough et al. (1976)
Urban (Zürich)				1500 ^f	Leuenberger et al. (1988)
Ward Creek, Sierra Nevada, CA		0.45–0.59			McConnell et al. (1998)
Lower Kaweah, Sierra Nevada, CA		1.7–9.4			McConnell et al. (1998)
Bothnian Bay (Baltic Sea)	0.5–1.4	0.18	60		Rahm et al. (1995)

^aSum of seven congeners (Fig. 4).

^bSum of α -HCH and γ -HCH.

^cSum of 22 parent compounds (all those included in Fig. 2 except retene).

^dBDL, below detection limit.

^eBQL, below quantification limit.

^fQuantified as Aroclor mixtures

^gPCB 28 and 153 not included.

^hSum of 10 compounds.

2.4. Quality control

All material, including snow cores and snow containers, was pre-rinsed with Milli-Q water and acetone before use. In addition, series of field and procedural blanks were performed at each sampling site and processed together with the samples. For field blanks, stainless-steel containers were filled with Milli-Q water for more than 2 h, filtered and solid phase adsorbed in parallel to the real samples, transported and stored for subsequent analysis. Blank values represented between 2 and 5% of snow levels. Analytical procedure recoveries were evaluated using the surrogate standards. Average recoveries for anthracene-d₁₀, pyrene-d₁₀, benzo[ghi]perylene-d₁₂, PCB congeners nos. 30 and 209 were 45 ± 11, 56 ± 5, 68 ± 10, 55 ± 14 and 80 ± 5%, respectively.

3. Results and discussion

Nine snow samples (snow layers and snow cores encompassing total snow package) were taken in undisturbed catchment areas of five remote lakes in Europe (Fig. 1). Samples were collected before any snow melting. At the Jöri site, two different snow layers and the whole snowpack were taken. Details on the sampling sites and meteorological conditions are given in Table 1. All but one sample represent the pollutant accumulation during winter 1997–98. Samples from Gossenkölle correspond to the accumulation during 1996–97. Collection of two snow cores at the same point in the catchment of Gossenkölle in March-97 and middle of May-97 allowed the estimation of intra-annual changes.

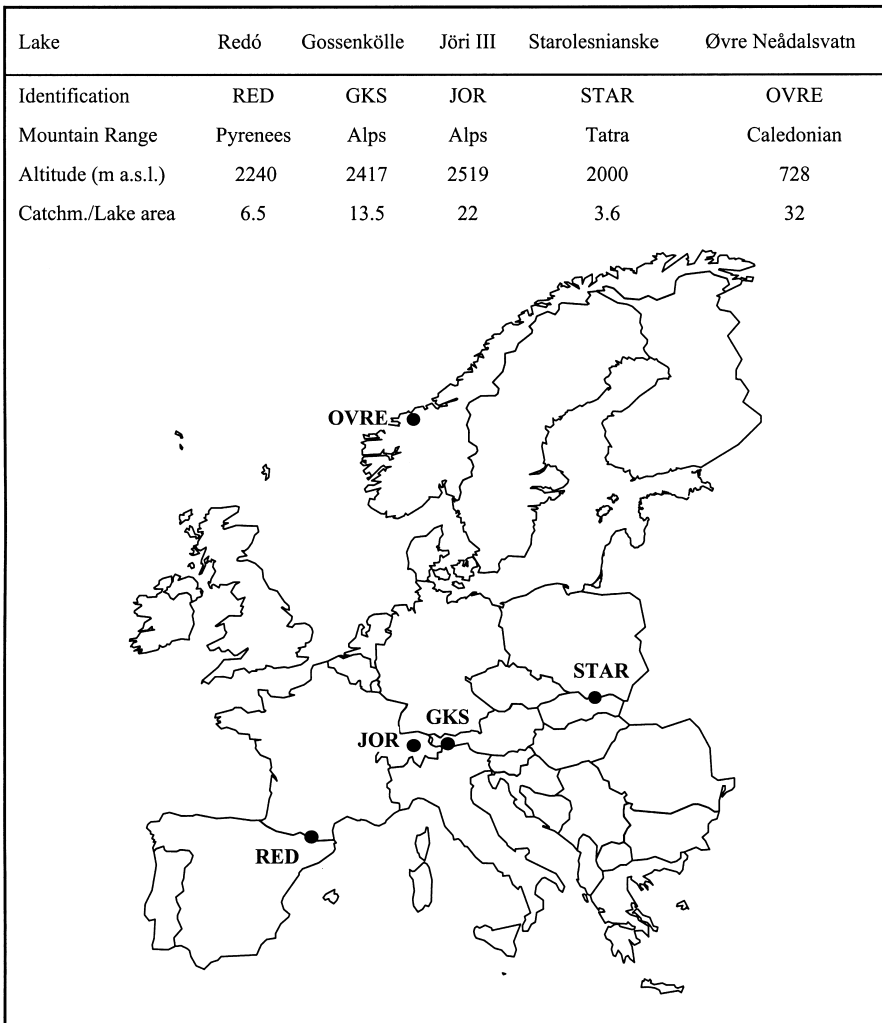


Fig. 1. Location of the sampling sites.

As indicated in the experimental section, the dissolved and particulate fractions of snow melt were analysed separately. However, during the melting process redistributions of contaminants between these two phases are known to occur. Melt snow does not necessarily reflect the distribution of chemicals in the original snow fractions nor the state of the compounds during their scavenging from the atmosphere (Wania et al., 1999). Thus, in the present study the identified pollutants are reported and discussed jointly. The concentrations determined independently in each of the two phases have been summed and they are reported as total values.

3.1. Polycyclic aromatic hydrocarbons

PAH with 3–7 aromatic rings were determined in the snow samples. The PAH patterns are generally dominated by phenanthrene. Fluoranthene and pyrene are the second major compounds (Fig. 2). This uniform pattern is observed at all sites except at Starolesnianske where fluoranthene is the major PAH. The snow collected at this site is also characterized by significant concentrations of other parent PAH such as benzo[ghi]fluoranthene, benz[a]anthracene, chrysene + triphenylene, benzo[b + j + k]fluoranthenes, benzo[e]pyrene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene.

Similar PAH distributions have been reported in the particulate phase of brown snow events in the Canadian Arctic (Welch et al., 1991) and in the catchment area of Lake Siskiwit (USA) (Mc Veety and Hites, 1988). These two cases involve transport of these pollutants to remote sites, as in the European sites considered in the present study. Conversely, PAH distribution in fresh snow and rain of urban locations show a different pattern with dominance of fluoranthene and pyrene and a higher proportion of the heavier molecular weight compounds (Franz and Eisenreich, 1998; Leuenberger et al., 1988).

In the atmosphere, the major compounds found in the remote European sites are usually present in the gaseous phase (Vilanova et al., 1998). They exhibit higher concentrations than the heavier PAH which dominate the particulate fraction. Vapour compounds are not removed as efficiently as those that are associated with aerosols (Dickhut and Gustafson, 1995; Franz and Eisenreich, 1998; Mc Veety and Hites, 1988). Gas scavenging by snow has been reported to be a minor contribution to PAH deposition, accounting for less than 10% (Franz and Eisenreich, 1998). However, in other studies gas scavenging has been described as an important, if not the dominant, snow scavenging process, due to the potentially large surface area of snow flakes and the tendency of semivolatile organic compounds such as the light PAH to associate with the air–ice interface (Wania et al., 1999). Due to the low temperatures, light PAH can condense on the atmospheric particles during transport to cold areas,

increasing their concentration in the particulate phase and, subsequently, their deposition by rain and snow. In addition, there is an exponential increase of the gas washout coefficient as air temperature decreases, which is mainly due to the decrease of the Henry's law constant with temperature (Dickhut and Gustafson, 1995). Thus, PAH gas washout may be more important in high altitude sites, enhancing the deposition of low molecular weight compounds.

The higher proportion of heavier PAH in Lake Starolesnianske, and to a lesser extent in Øvre Neadålsvatn (Fig. 2), can be explained by the higher amount of particles detected in the snow from these lakes (2.0 and 2.3 mg l⁻¹, in Starolesnianske and Øvre Neadålsvatn-98, respectively; Table 1). However, the snow core taken in Øvre Neadålsvatn in 1997 also shows a PAH composition enriched in heavier compounds but its particle content is in the range of the other lakes (1.0 mg l⁻¹). On the other hand, the highest particle concentrations are observed in one core of Jöri III but this is not enriched in heavier PAH. In any case, this pattern is very similar to that found in the surface sediment cores of most high-altitude lakes in Europe (Fernandez et al., 1996, 1999). Thus, snowfall may constitute a feasible mechanism for the incorporation of these compounds from air to lake sediments.

On the other hand, the snow samples with higher proportions of heavier molecular weight compounds are also those with higher PAH concentrations. The concentrations of PAH_{tot} in Starolesnianske and Øvre Neadålsvatn are 81 and 32 ng l⁻¹, respectively, whereas in the rest of the samples range from 5.6 (Redó) to 17 ng l⁻¹ (Gossenkölle) (see Table 2 and Fig. 3). No correspondence has been found between winter precipitation or air temperature and concentrations of PAH_{tot} in snow from different lakes.

PAHs in samples from the same sites but different years (Øvre Neadålsvatn and Jöri) show similar qualitative distribution and small concentration differences (Figs. 2 and 3). Thus, in Jöri, PAH_{tot} ranged between 27 (surface) and 21 ng l⁻¹ (50–70 cm layer) in 1997, whereas the average composition of the snow core was 16 ng l⁻¹ in 1998. In Øvre Neadålsvatn, the average PAH_{tot} in the snowpack were 25 and 32 ng l⁻¹ in 1997 and 1998, respectively. These differences could reflect different precipitation amounts between these years. Higher precipitation was measured in Jöri in 1997 than in 1998 (Table 1).

The snow PAH concentrations can be expressed as annual-accumulation rates (Fig. 3) multiplied by water equivalents (Table 1) and rating to total-annual precipitation (Table 1). This rating can be performed using Table 1 data. Thus, deposition values were multiplied by the annual snow precipitation (total precipitation × percent snow precipitation) and divided by sample precipitation. Starolesnianske exhibits the highest values with

a PAH accumulation of $3.7 \text{ ng cm}^{-2} \text{ yr}^{-1}$, followed by Øvre Neadålsvatn with $2.7 \text{ ng cm}^{-2} \text{ yr}^{-1}$, Gossenkölle with $1.2 \text{ ng cm}^{-2} \text{ yr}^{-1}$, Jöri with $1.4 \text{ ng cm}^{-2} \text{ yr}^{-1}$, and finally Redó with the lowest value of $0.42 \text{ ng cm}^{-2} \text{ yr}^{-1}$. The two snow cores collected in Gossenkölle indicate rather uniform rates in PAH deposition since their similar PAH concentrations (Fig. 3) correspond to annual accumulation rates of $1.2 \text{ ng cm}^{-2} \text{ yr}^{-1}$ in GKS-March and $1.3 \text{ ng cm}^{-2} \text{ yr}^{-1}$ in GKS-May (Table 3).

These values are of the same order of magnitude than those found in the surface sediments of high mountain lakes located in central and western Europe where the annual deposition rates range between 5.4 and $8.5 \text{ ng cm}^{-2} \text{ yr}^{-1}$ (Fernandez et al., 1999). In eastern Europe, where Starolesnianske is located, the ratio is lower, and it is the 2% of the annual-sedimentary deposition ($180 \text{ ng cm}^{-2} \text{ yr}^{-1}$; Fernandez et al., 1999).

Comparison between snow and sediment accumulation rates is not straightforward since many processes influence PAH transfer to lake sediment. One dominant aspect for consideration is the influence of catchment. A substantial part of the pollutants accumulated in the snow collected in the catchment may be incorporated into the lake. Normalization of the snow deposition fluxes to lake area (multiplication by the catchment lake area ratio; Fig. 1) affords a rough estimate to account for this effect. Strong differences between lakes are observed when considering this aspect (Table 3). Thus, in Øvre Neadålsvatn and Gossenkölle the snow deposition fluxes 86 and $16 \text{ ng cm}^{-2} \text{ yr}^{-1}$, respectively, are higher than the fluxes to sediment, 7.1 and $5.4 \text{ ng cm}^{-2} \text{ yr}^{-1}$, respectively. Obviously, not all PAH trapped in the catchment snow are incorporated into the lake but these figures suggest that a substantial part of PAH pollution enters into the lake in association to falling snow. In contrast, in Starolesnianske, the normalized snow deposition values are still very low in comparison to the sediment fluxes pointing to a small influence of snow transport for the incorporation of PAH load. Lake Redo probably represents an intermediate situation.

3.2. Organochlorine compounds

Four organochlorine pollutant classes have been found in the snow samples, namely polychlorinated biphenyls (PCB), hexachlorocyclohexanes (α -HCH and γ -HCH), hexachlorobenzene (HCB), and DDTs (4,4'-DDE

and 4,4'-DDT). DDTs were only detected in concentrations above quantitation limit (47 pg l^{-1}) in the snow from Starolesnianske (73 pg l^{-1}) and Gossenkölle (330 pg l^{-1}). No 4,4'-DDE was found above the detection limit. HCB was present in a limited number of samples, Øvre Neadålsvatn-97 (48 pg l^{-1}), Starolesnianske (7.1 pg l^{-1}) and Redó (10 pg l^{-1}). The levels in the two latter lakes are close to quantitation limit (6.6 and 9.2 pg l^{-1} , respectively). The discussion will be therefore focussed on PCB and HCH, the compounds above quantitation limit in all samples.

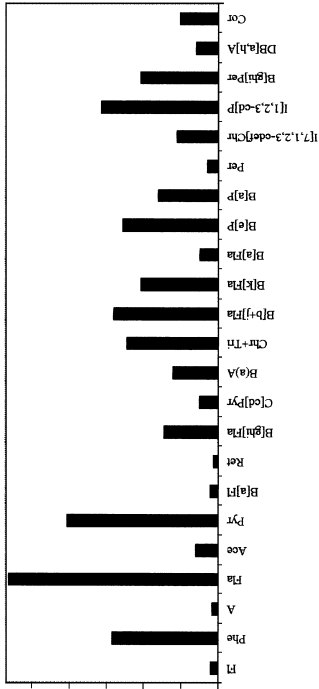
The PCB congener distributions are different in each site (Fig. 4). Snow from Jöri and, to a lesser extent, Gossenkölle, presents a higher proportion of less volatile compounds. In contrast, the higher proportion of the more volatile compounds is found in Redo and Øvre Neadålsvatn. Starolesnianske represents an intermediate situation. No significant differences have been detected between the two snow cores collected in Gossenkölle, nor between the surface and deep snow samples from Jöri, though PCB 180 was not detected in the surficial snow layer.

PCBs are present in the atmosphere mainly in the gas phase. Vapour PCB account for 90% of total atmospheric content, up to 99% for the most volatile compounds (Duinker and Bouchertall, 1989). However, particle scavenging has been described as the dominant source of PCB in deposition samples, so higher contribution of more than less-chlorinated congeners would be expected in PCB mixtures from snow samples.

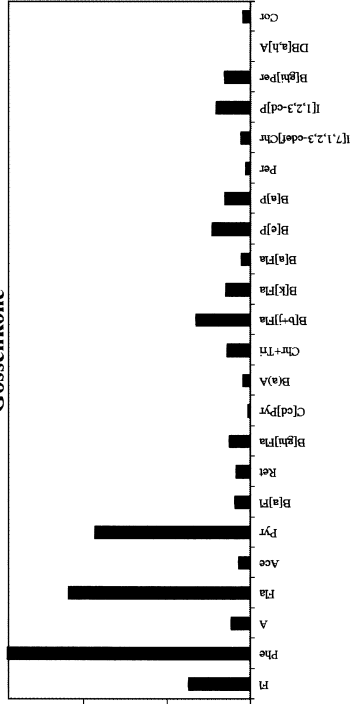
Similar PCB distributions have been reported in snow from remote sites (Tanabe et al., 1983; Swackhamer et al., 1988). Distance from the sources and the long residence times in the atmosphere of vapour-phase PCBs have been proposed as likely causes of this PCB pattern. Blais et al. (1998) reported an increase in snow concentration of the most volatile PCB with increasing altitude in the Canadian Rocky mountains, in agreement with the cold-condensation hypothesis (Wania and Mackay, 1993). This trend has not been observed in our study. However the narrow altitude range of Fig. 1 sites (most of them among 2000–2500 m a.s.l.) and their different average air temperature range (average winter temperature between -0.5 and -5.3°C) involve other climatic conditions than those observed in the Canadian mountain study (January average temperatures between -8 and -18°C).

Fig. 2. Distributions of polycyclic aromatic hydrocarbons in snow samples from remote mountain sites. Compound identification: (Fl) fluorene, (Phe) phenanthrene, (A) anthracene, (Fla) fluoranthene, (Ace) acephenanthrylene, (Pyr) pyrene, (B[a]Fl) benzo[a]fluorene, (Ret) retene, (B[ghi]Fla) benzo[ghi]fluoranthene, (C[cd]Pyr) cyclopenta[cd]pyrene, (B[a]A) benz[a]anthracene, (Chr + Tri) chrysene + triphenylene, (B[b + j]Fla) benzo[b + j]fluoranthene isomers, (B[k]Fla) benzo[k]fluoranthene, (B[a]Fla) benzo[a]fluoranthene, (B[e]P) benzo[e]pyrene, (B[a]P) benzo[a]pyrene, Per perylene, (I[7,1,2,3-cdef]Chr) indeno[7,1,2,3-cdef]chrysene, (I[1,2,3-cd]P) indeno[1,2,3-cd]pyrene, (B[ghi]Per) benzo[ghi]perylene, (DB[ah]A) dibenz[ah]anthracene, Cor coronene.

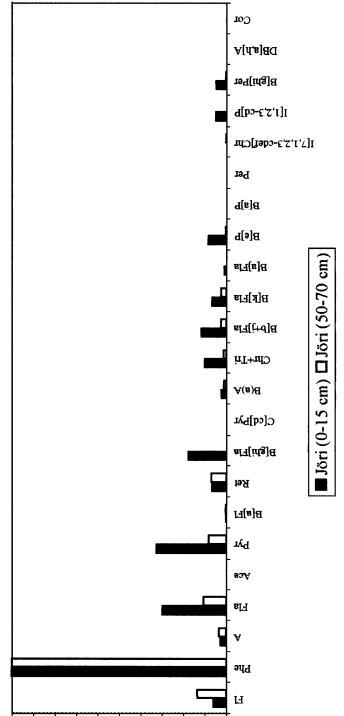
Starolesnianske



Gossenkölle



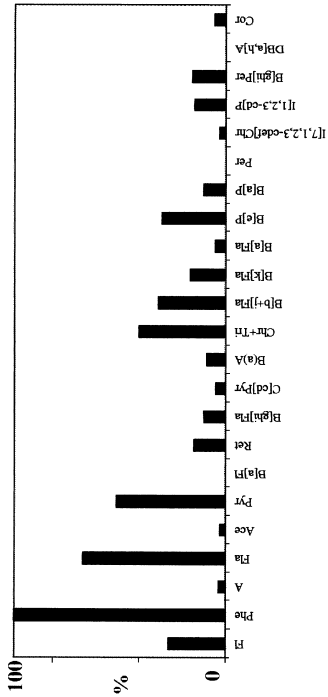
Jöri-97



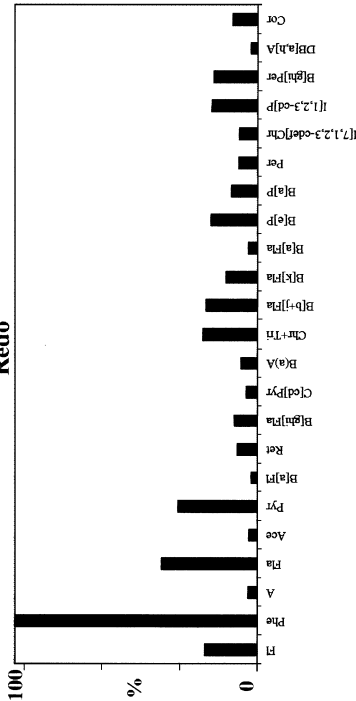
PAH

■ Jöri (0-15 cm) □ Jöri (50-70 cm)

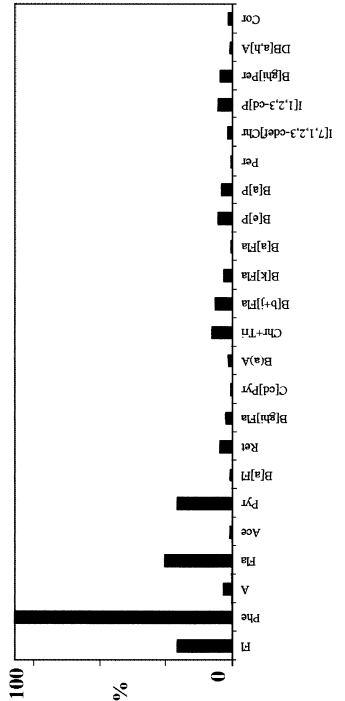
Øvre Neadalsvatn



Redó



Jöri-98



PAH

■ Jöri (0-15 cm) □ Jöri (50-70 cm)

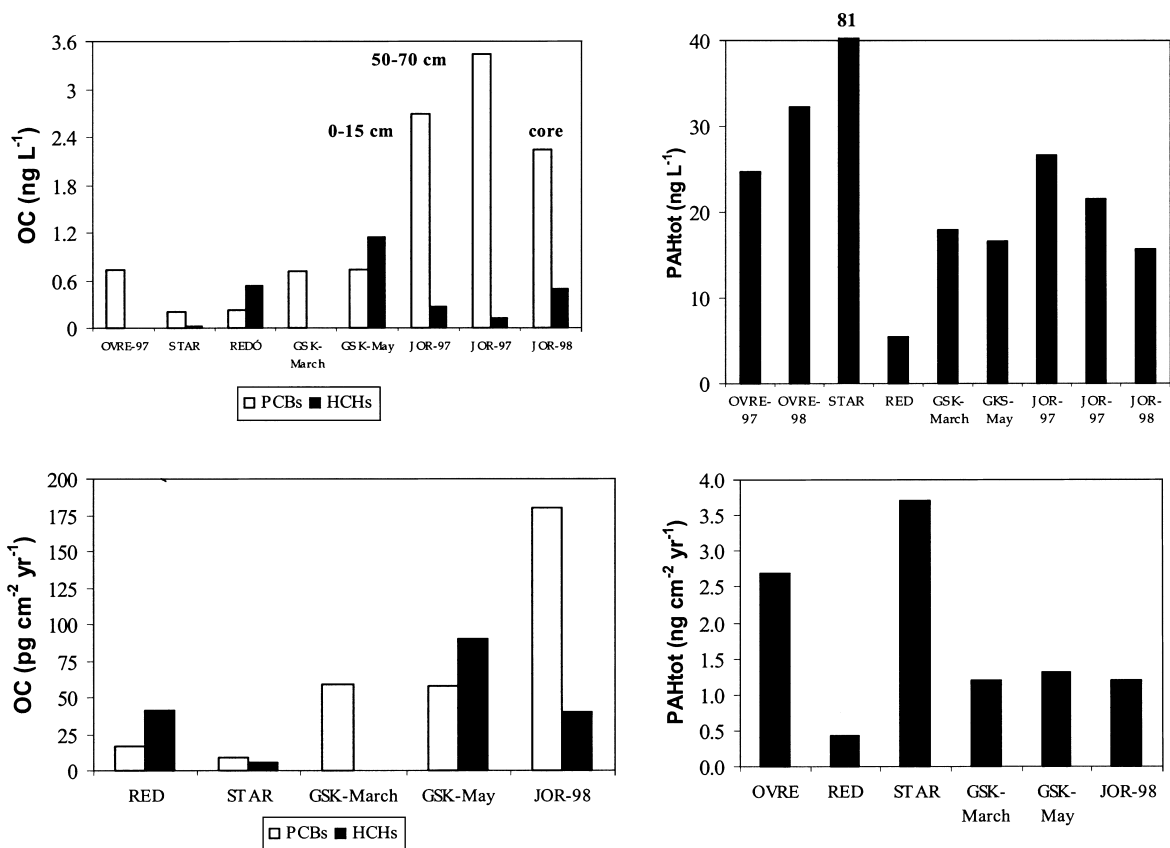


Fig. 3. Concentrations and annual deposition fluxes of PAH_{tot} (sum of 22 parent compounds), PCB (sum of seven congeners), and HCH (sum of α - and γ -HCH) in snow from the study areas. Lake identification in Table 1.

Table 3

Comparison of PAH deposition fluxes in snow and sediment from some European high mountain lakes

Site	Snow deposition ^a (ng cm ⁻² yr ⁻¹)	Sediment deposition ^b (ng cm ⁻² yr ⁻¹)	Snow deposition normalized to catchment ^c (ng cm ⁻² yr ⁻¹)
Gossenkölle	1.25	5.4	16
Redó	0.42	8.5	2.7
Starolesnianske	3.7	180	13
Ovre Neadalsvatn	2.7	7.1	86

^aCalculated as concentration \times (water equivalents \times annual precipitation \times % snow precipitation/sample precipitation) from the date of Tables 1 and 2.

^bData from Fernandez et al. (1999).

^cCalculated as snow deposition \times ((lake + catchment) area/lake area).

The highest PCB concentrations are found in the Alps (2.2 ng l⁻¹ in Jöri and 0.73 ng l⁻¹ in Gossenkölle) whereas the lowest are observed in the Tatras (Starolesnianske, 0.20 ng l⁻¹) and the Pyrenees (Redó, 0.22 ng l⁻¹). Taking

into consideration the different quantitation methods used for determining PCB content in snow samples in the literature (individual congeners versus Aroclor mixtures), the concentrations found in the present

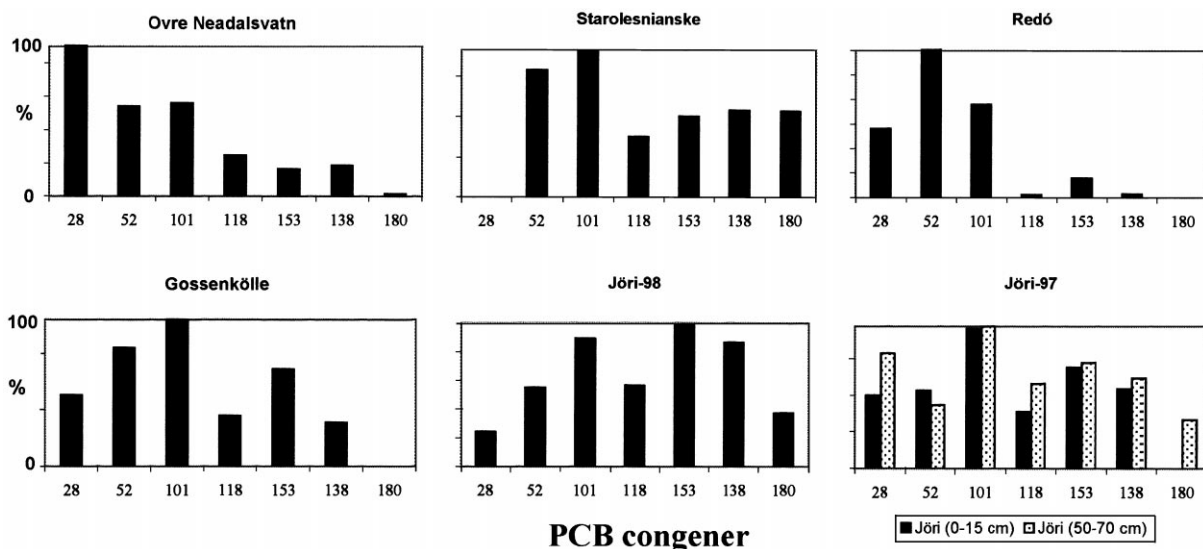


Fig. 4. Distributions of polychlorinated biphenyl congeners in snow from remote mountain sites. The following PCB congeners coelute total or partially in the chromatographic conditions applied in this study: 28 + 31, 101 + 84 and 138 + 160 + 163.

study, namely those from the Alps sites, are in the upper range of those reported for other remote regions such as Antarctica, the Arctic, and mountainous areas (Table 2).

Transformation of these concentrations in PCB annual accumulation rates gives rise to similar differences between sites (Fig. 3). The highest levels are found in Jöri ($180 \text{ pg cm}^{-2} \text{ yr}^{-1}$) and Gossenkölle ($59 \text{ pg cm}^{-2} \text{ yr}^{-1}$) and the lower in Redó ($17 \text{ pg cm}^{-2} \text{ yr}^{-1}$) and Starolesnianske ($8.8 \text{ pg cm}^{-2} \text{ yr}^{-1}$).

HCH have been found in all samples but in Øvre Neadalsvatn. In general, γ -HCH is the only detected isomer, in agreement to the general phasing out of the technical mixture of this pesticide in Europe (Voldner and Li, 1995). α -HCH has only been detected in Redó where it occurs in low amount with respect to the γ -isomer. The highest values of this pollutant are found in Gossenkölle and Redó (Table 2, Fig. 3). However, the levels are lower than those reported in other remote ecosystems (Table 2).

In Contrast to PCB and PAH, major differences in the case of HCH are observed between samples collected at the same site during different periods. Although an assessment of the possible factors determining temporal variability is beyond the scope of the present study, the strong changes recorded in Gossenkölle are in agreement with the seasonal application of this pesticide in relation to agricultural activities giving higher deposition episodes in spring–summer than winter (Wania and Haugen, 1999).

4. Conclusions

PAH, PCB and HCH are found in all snow samples collected in remote high mountain European sites. Despite the predominance of atmospheric mechanisms for the transport of these compounds to these high-altitude sites, their concentrations in snow do not exhibit parallel geographic distributions. Thus, PAH are found in higher amounts in the Tatra and Caledonian mountains, PCB in the Alps and HCH in the Alps and Pyrenees.

Some of the major compounds found in the snow samples, e.g. HCH and low molecular weight PAH and PCB, occur predominantly in the gas phase. Their high abundance in the snowpack witness the occurrence of effective transfer mechanisms from gas to snow flakes.

PAH composition in snow is similar to that found in the sediments of the high-altitude lakes situated near the sampling sites. Thus, its qualitative distribution is very uniform in all mountain regions. Transformation of concentration values into annual deposition rates and correction for catchment/lake area indicates that in Scandinavia and the Alps a large proportion of PAH incorporation is mediated by snow fallout whereas that in the Tatra mountains snow may account for a small fraction (< 10%) of the compounds found in the lake sediments. The Pyrenees probably represent an intermediate situation.

Preliminary comparison between samples collected at different seasons shows a remarkable uniformity for the qualitative and quantitative snowpack composition of

PAH and PCB. In contrast, HCH exhibit major variations which may parallel agricultural uses.

Acknowledgements

We thank Ulrike Nickus (University of Innsbruck), Marc Ventura (University of Barcelona), Leif Lien (NIVA, Norway), Ezven Stülich (University of Prague), David Livingstone (EAWAG, Dübendorf), Beatrice Steiner (University of Bern), and Matthias Gabathuler (ETH of Zürich) for snow samples and meteorological data. Roser Chaler (Department of Environmental Chemistry, ICER-CSIC) is acknowledged for technical assistance in instrumental analysis. This work was funded by the Commission of the European Communities through the Mountain Lake Research (MOLAR) project (ENV4-CT95-0007). R.M.V. acknowledges financial support from the Spanish Ministry of Education.

References

- AMAP, 1998. www.amap.no
- Blais, J.M., Schindler, D.W., Muir, D.C.G., Kimpe, L.E., Donald, D.B., Rosenberg, B., 1998. Accumulation of persistent organochlorine compounds in mountains of Western Canada. *Nature* 395, 585–588.
- Carrera, G., Fernández, P., Vilanova, R., Grimalt, J.O., 1998. Analysis of trace polycyclic aromatic hydrocarbons and organochlorine compounds in atmospheric residues by solid-phase disk extraction. *Journal of Chromatography* 823, 189–196.
- Dickhut, R.M., Gustafson, K.E., 1995. Atmospheric washout of polycyclic aromatic hydrocarbons in the Southern Chesapeake Bay region. *Environmental Science and Technology* 29, 1518–1525.
- Duinker, J.C., Bouchertall, F., 1989. On the distribution of atmospheric polychlorinated biphenyls congeners between vapour phase, aerosols, and rain. *Environmental Science and Technology* 23, 57–62.
- Fernandez, P., Vilanova, R., Grimalt, J.O., 1996. PAH distributions in sediments from high mountain lakes. *Polycyclic Aromatic Compounds* 9, 121–128.
- Fernández, P., Vilanova, R., Grimalt, J.O., 1999. Sediment fluxes of polycyclic aromatic hydrocarbons in European high altitude mountain lakes. *Environmental Science and Technology* 33, 3716–3722.
- Franz, T.P., Eisenreich, S.J., 1998. Snow scavenging of polychlorinated biphenyls and polycyclic aromatic hydrocarbons in Minnesota. *Environmental Science and Technology* 32, 1771–1778.
- Franzén, L.G., Hjelmroos, M., Kallberg, P., Brorström-Lundén, E., Junto, S., Savolainen, A.-L., 1994. The “Yellow Snow” episode of Northern Fennoscandia, March 1991 – a case study of long-distance transport of soil pollen and stable organic compounds. *Atmospheric Environment* 28, 3587–3604.
- Gregor, D.J., Gummer, W.D., 1989. Evidence of atmospheric transport and deposition of organochlorine pesticides and polychlorinated biphenyls in Canadian Arctic snow. *Environmental Science and Technology* 23, 561–565.
- Hoff, J.T., Wania, F., Mackay, D., Gillham, R., 1995. Sorption of nonpolar organic vapors by ice and snow. *Environmental Science and Technology* 29, 1982–1989.
- Jaffrezou, J.L., Clain, M.P., Masclet, P., 1994. Polycyclic aromatic hydrocarbons in the polar ice of Greenland. Geochemical use of these atmospheric tracers. *Atmospheric Environment* 28, 1139–1145.
- Leuenberger, C., Czuczwa, J., Heyerdahl, E., Giger, W., 1988. Aliphatic and polycyclic aromatic hydrocarbons in urban rain snow and fog. *Atmospheric Environment* 22, 695–705.
- Mc Veety, B.D., Hites, R.A., 1988. Atmospheric deposition of polycyclic aromatic hydrocarbons to water surfaces: a mass balance approach. *Atmospheric Environment* 22, 511–536.
- McConnell, L.L., LeNoir, J.S., Datta, S., Seiber, J.N., 1998. Wet deposition of current-use pesticides in the Sierra Nevada Mountain Range California, USA. *Environmental Toxicology and Chemistry* 17, 1908–1916.
- Patton, G.W., Hinckley, D.A., Walla, M.D., Bidleman, T.F., Hargrave, B.T., 1989. Airborne organochlorines in the Canadian High Arctic. *Tellus* 41B, 243–255.
- Rahm, L., Hakansson, B., Larsson, P., Fogelqvist, E., Bremle, G., Valderrama, J., 1995. Nutrient and persistent pollutant deposition on the Bothnian Bay ice and snow fields. *Water, Air, Soil Pollution* 84, 187–201.
- Risebrough, R.W., Walker, W.I., Schmidt, T.T., Delappe, B.W., Connors, C.W., 1976. Transfer of chlorinated biphenyls to Antarctica. *Nature* 264, 738–739.
- Swackhamer, D.L., McVeety, B.D., Hites, R.A., 1988. Deposition and evaporation of polychlorobiphenyls congeners to and from Siskiwit Lake, Isle Royale, lake Superior. *Environmental Science and Technology* 22, 664–672.
- Tanabe, S., Hidake, H., Tatsukawa, R., 1983. PCB and chlorinated hydrocarbons pesticides in Antarctic atmosphere and hydrosphere. *Chemosphere* 12, 277–288.
- Vilanova, R., Fernandez, P., Grimalt, J.O., 1998. Atmospheric persistent organic pollutants in high altitude mountain lakes. A preliminary study. In: Pacyna, J.M., Broman, D., Lipiatou, E. (Eds.), *Sea–Air Exchange: Processes and Modelling*. Office for Official Publications of the European Communities, Luxembourg, pp. 209–215.
- Voldner, E.C., Li, Y.-F., 1995. Global usage of selected persistent organochlorines. *Science of the Total Environment* 160/161, 201–210.
- Wania, F., Haugen, J.-E., 1999. Long term measurements of wet deposition and precipitation scavenging of hexachlorocyclohexanes in Southern Norway. *Environmental Pollution* 105, 381–386.
- Wania, F., Hoff, J.T., Jia, C.Q., Mackay, D., 1998. The effects of snow and ice on the environmental behaviour of hydrophobic organic chemicals. *Environmental Pollution* 102, 25–41.
- Wania, F., Mackay, D., 1993. Global fractionation and cold condensation of low volatility organochlorine compounds in polar regions. *Ambio* 22, 10–18.
- Wania, F., Mackay, D., Hoff, J.T., 1999. The importance of snow scavenging of polychlorinated biphenyl and polycyclic aromatic hydrocarbon vapors. *Environmental Science and Technology* 33, 195–197.
- Welch, H.E., Muir, D.C.G., Billeck, B.N., Lockhart, W.L., Burnskill, G.J., Kling, H.J., Olson, M.P., Lemoine, R.M., 1991. Brown snow: a long-range transport event in the Canadian Arctic. *Environmental Science and Technology* 25, 280–286.