

Distribution of polychlorinated biphenyls (PCBs) in snow samples in northern Norway

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Introduction

Snow and ice play an important role in the hydrological cycle of Northern countries. It is well known that persistent organic pollutants (POPs) are transported in the atmosphere over long distances. There are indications that some POPs, such as certain organochlorinated pesticides and polychlorinated biphenyls (PCBs) preferentially deposit and accumulate in cold regions. The presence of snow and ice strongly influences the behavior of POPs in Northern environments by modifying chemical cycling between the atmosphere and the Earth's surface. Therefore an extensive and quantitative understanding of the interaction between these chemicals and snow/ice is required for an assessment and evaluation of their environmental fate and behavior in Northern ecosystem. Of particular interest is to investigate the fate of contaminants in a snow pack during the aging process during which the snow experiences changes in its physical characteristics such as temperature, density, surface area and particle content. Such investigation includes the question to what extent a chemical scavenged from the atmosphere is re-emitted to the atmosphere, and to what extent it is transferred to the underlying surface during melting. To gain reliable information of the PCBs and their fate in the snowpack, it is of great importance that the sampling site is not influenced by local contamination during the sampling period. In addition loss of contaminants during the melting of the snow samples should be avoided.

Material and Methods

For the presented preliminary study, a sampling site located at Frihetsli, Dividalen in Troms county (northern Norway) was chosen. This area is not influenced by any substantial local contamination and therefore considered as background station. Inland sampling sites are preferable due to the good predictability of meteorological conditions compared to coastal regions. The Norwegian Meteorological Institute provides data for the sampling site received on a monthly basis. Therefore, weather conditions can be considered and linked to the analytical results. The concentration of PCBs in snow at several meteorological occasions was measured. Surface snow and melt water were sampled during the winter 1997/98. Due to low concentration of PCBs expected, sufficient sample volume was needed. Therefore, a 50 liter

container was chosen for snow sampling. The sample containers were kept gas tight after sampling in order to prevent potential evaporative loss. At the field site, the melt water was collected with stainless steel snow lysimeters (figure 1).

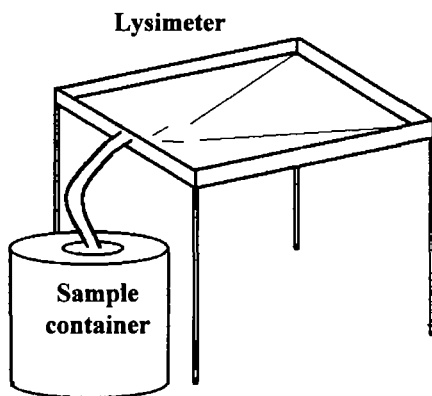


Figure 1: Lysimeter at the sampling site (1 m^2). Melted snow is transferred from the lysimeter, through stainless steel tubes to the gas tight 50 L containers.

All sampling equipment was carefully cleaned at the sample site with methanol to avoid contamination. Solvents used for the sample preparation were SupraSolv quality purchased from Merck (Darmstadt, Germany). For extraction, the sample container was connected to a stainless steel extraction cartridge. The cartridge contains a polyurethane foam (PUF) plug and a glass microfibre (GM) filter with poresize $2\text{ }\mu\text{m}$ (multigrade GMF ISO, Whatman, USA). The PUF plug extracts the PCBs dissolved in the water phase whereas the GM filter collects the PCBs in the particle phase. PCB 54 as internal standard (IS) was added to the PUF plug. The melt water was transferred through the extraction cartridge under low nitrogen pressure (N_2 , quality 5.0). A low flow rate of about 3-4 L/min. was chosen to avoid unexpected breakthrough. After extraction, the PUF plug and the GM filter were transferred to 100 ml of n-hexane and acetone (1:1) and extracted for 15 min. in ultra sonic bath (Branson Ultrasonics B.V., UK). The extraction was repeated. The two subsequent extracts were unified and transferred into a separation funnel. The separation funnel was shaken for 2-3 minutes. After shaking, the water/acetone and n-hexane phase separates after 1-2 minutes completely. The water/acetone phase was removed and the n-hexane phase was concentrated to 1-2 ml for further clean-up. The concentrated extract was treated with 2 ml of 99 % sulfuric acid (Merck, Darmstadt, Germany, p.a quality). The n-hexane phase was transferred to a 2 ml glass vial and concentrated to 500 μl . A column chromatographic clean-up was performed with 4 g silica (0.063-0.200 mm, Merck, Germany) in a glass column (ID: 1 cm; Length: 10 cm). The silica was heated to 600°C for 6 hours prior to use. The sample was eluted with 30 ml n-hexane. After the clean-up, a recovery standard (octa chloro naphthalene) was added. The extract was concentrated to 200 μl and the PCB content was determined. The analyses were performed on a Fisons Mega II GC (Milan, Italy) coupled to a MD 800 low resolution mass spectrometric

detector (Finnigan, San Jose, CA) in electron impact mode (EI). The sample was injected on-column with a Fisons autosampler (AS800). A fused silica capillary column (HP5MS, length: 25 m; ID: 0.25 mm; Film thickness: 0.25 μ m, Hewlett Packard, Oslo, Norway) coupled to a 2 meters fused silica guard column (ID: 0.53 mm, J&W, Folsom, CA, USA) was used for the gas chromatographic separation. Helium was chosen as carrier gas (quality 5.0; Flow rate: 1 ml/minute). The quantification was carried out in single ion recording (SIR). During analysis, the ion source and the interface temperatures were 180°C and 250°C, respectively. The measurements were carried out with an ion energy of 70 eV. In addition to the quantification, isotope ratios (IR) between quantification and reference masses were determined in the sample and the quantification standard. A deviation of more than 30 % compared to the IR of the quantification standard leads to rejection of the results. The following temperature program was used for PCB analysis: 60°C, (2 min. isothermal), 15°C/min until 180°C, 5°C/min. until 250°C and 15°C/min until 280°C (10 min. isotherm). The PCBs analysed are listed in table 1.

Table 1: PCB congeners analysed in the presented snow samples, including quantification and reference masses and detection limits. Abbreviations: Quant. mass: quantification mass, ref. Mass: reference mass.

PCB congener	IUPAC-nomenclature	Quant. Mass	Ref. Mass
28	<i>2,4,4'-trichlorobiphenyl</i>	258	256
52	<i>2,2',5,5'-tetrachlorobiphenyl</i>	292	290
118	<i>2,3,4,4',5-pentachlorobiphenyl</i>	326	328
126	<i>3,3',4,4',5-pentachlorobiphenyl</i>	326	328
138	<i>2,2',3,4,4',5-hexachlorobiphenyl</i>	360	362
149	<i>2,2',3,4',5,6- hexachlorobiphenyl</i>	360	362
153	<i>2,2',4,4',5,5'- hexachlorobiphenyl</i>	360	362
169	<i>3,3',4,4',5,5'- hexachlorobiphenyl</i>	360	362
180	<i>2,2',3,4,4',5,5'-heptachlorobiphenyl</i>	394	396
187	<i>2,2',3,4',5,6,6'- heptachlorobiphenyl</i>	394	396

Results and Discussion

Lysimeters and containers for melt water collection were installed in the beginning of November 1997. Since wet deposition mainly occurred as rain during the last two months of the year, containers were replaced late January 1998. Surface snow was collected in early March. The concentrations levels obtained by GC/MS analyses of the snow are clearly below the concentrations found in precipitation from southern Norway¹. These levels are also much lower than the PCB burden found in fresh surface snow and snowpacks in the Canadian Arctic² and in Taimyr Peninsula, Russia². Dividalen is therefore assumed to be an appropriate choice for monitoring of PCB background levels in the Arctic environment. All concentration values were found below the 1 ng/L level. However, due to interferences in the chromatogram, only a limited number of PCB congeners were analysed. Thus, optimisation of the method is still needed. Nevertheless, tendencies in different snow samples could be investigated. Differences in the PCB pattern of melted snow (sampled over a period of nearly 3 months) and surface snow collected near the sampling site was found. The concentration

range is comparable in meltwater and surface snow. However, the amount of high chlorinated PCBs are much lower in the surface snow. In general, compounds with relatively high vapour pressures can volatilise substantially from the snowpack, especially from the surface snow (20-30 cm) and in shallow snow packs. This effect is also enhanced during higher ambient temperature, in particular during spring time. Adsorption of organic pollutants to snow crystals may be quite different from rain scavenging. Nevertheless, it is too early to conclude if such differences are revealed here. Further information will be given in the presentation. These first results demonstrated the effectivity of the chosen method for back ground concentration levels.

Table 2: The typical distribution of the PCB-content of two selected integrated melt water samples and a surface snow sample, collected at Dividalen (Frihetsli: march 1998) in the period from november 1997 until february 1998. Abbreviations and marks: I = interferences in the chromatogram. *) Congeners which not exceed 3 times blank concentrations are marked with asterisk.

	Laboratory blank (30 L)	melt water 1 (30 L)	melt water 2 (50 L)	Snow surface (30 L)
Congeners	pg/L	pg/L	pg/L	pg/L
PCB 28	<0.4	I	I	325.3
PCB 52	87.9	550.0	252.3	92.3 *
PCB 118	<0.7	421.2	204.7	7.15
PCB 126	<0.6	I	I	3.24
PCB 138/163	<0.9	504.9	302.7	102.4
PCB 149	<0.9	368.8	184.4	387.8
PCB 153/132	<0.8	817.4	441.4	98.8
PCB 169	<0.7	598.5	I	I
PCB 180	<0.6	67.7	22.8	6.42
PCB 187	<1.4	259.5	84.1	I

Acknowledgements

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References

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