ORGANOCHLORINES, POLYBROMINATED DIPHENYL ETHERS AND PERFLUORINATED COMPOUNDS IN MARINE SEDIMENTS FROM ISFJORDEN, SVALBARD

Evenset, A[1], Christensen, GN[1] & Berger, U[2]

1 Akvaplan-niva, Polar Environmental Centre, 9296 Tromsø, Norway
2 Norwegian Institute for Air Research, Polar Environmental Centre, 9296 Tromsø, Norway

1 Introduction

Svalbard is a high-Arctic island group located about 1000 km north of the mainland of Norway. Despite its remote location and Arctic climate, there are and have been several human settlements on the island. Today there are two relatively large and one smaller active settlement based around mining activities on the island; Longyearbyen, Barentsburg and Svea. Two other settlements based on mining activities have been abandoned; Pyramiden (abandoned in 1998) and Colesbukta (abandoned in 1962).

It is a well known fact that Arctic areas, such as Svalbard, are recipients of contaminants transported through air and ocean currents from industrialised areas further south[1,2]. The fjord areas outside the settlements on Svalbard therefore receive contaminants both from long-range transport and from local sources. Potential local sources include mining operations, traffic (cars, snow scooters, ships), sewage and waste dumps. From previous studies it is known that the marine areas outside the settlements have higher concentrations of organochlorines than sediments from open sea areas around Svalbard[3, 4, 5]. However, to our knowledge no studies of currently used compounds, such as polybrominated diphenyl ethers (PBDEs) or perfluorinated alkyl substances (PFAS), have been carried out in these areas.

The main objective of the present study was to monitor levels of selected organochlorines in four coastal areas in the Isfjorden-complex potentially affected by local discharges from the settlements Longyearbyen (Adventfjorden), Barentsburg (Grønfjorden), Pyramiden (Billefjorden) and Colesbukta. In addition, one area that has been abandoned for more than 40 years, Colesbukta, was included in the study. A second goal was to present the first measurements of the current-used compounds PBDEs and PFAS in sediments from these areas.

2 Materials and methods

Field work: The sampling was carried out from *MS Nordsyssel* from 29. September – 1. October 2005. Eight sediment samples were collected from each area (Figure 1) with a 0.1 m^2 Van Veen grab. The surface sediment (0 – 1 cm) was transferred to burned glass-jars and frozen on board to -20 °C.

***Analyses*:** Eight samples from each of the three fjords Adventfjorden, Grønfjorden and Billefjorden were included in the analytical programme, whereas only three samples from Colesbukta were analysed. 12 polychlorinated biphenyl (PCB) congeners (CB 28, 52, 99, 101, 105, 118, 138, 153, 180, 183, 187 and 194), hexachlorbenzene (HCB), dichlorodiphenyltrichlorethane (DDT) and metabolites (o,p'-DDD, o,p'-DDE, p,p'-DDE, o,p'-DDT and *p,p'*-DDT) were quantified in all the samples. In addition, 8 PBDE-congeners (BDE 47, 99, 100, 138, 153, 154, 183 and 209) and 10 PFCs (PFBS, PFHxS, PFOS, PFDcS, PFHpA, PFOA, PFNA, PFDcA, PFUnA and PFDoA) were quantified in 8 samples (Table 2). All analyses were carried out by the Norwegian Institute for Air Research.

TOC and grain size: Total organic carbon (TOC) was determined using a Leco IR 212 carbon analyser. Grain size (<> 63 µm) was determined by wet sieving.

PCBs, HCB, DDTs and PBDEs: 10 – 50 g freeze-dried sediment was spiked with ^{13}C-labelled internal standard solution. Soxhlet extraction of the sediment samples was performed with toluene at reflux for 8 hours. The toluene extract was concentrated to 0.5 mL while changing the solvent to dichloromethane. Sulphur was removed by gel permeation chromatography. The fraction between 75 and 106 mL was collected and concentrated to 0.5 mL (Turbovap) while changing the solvent to cyclohexane. The extract was additionally cleaned up using a florisil column. Gas chromatography

coupled to mass spectrometry (GC/MS) was employed for separation and quantification of all analytes, with the exception of PFAS.

PFAS: 2.5 g freeze-dried material was spiked with internal standard and extracted on a shaking device for 30 minutes. Aliquots of freeze-dried material were cleaned with ENVI-Carb. High resolution liquid-chromatography-mass-spectrometry (LC/MS-TOF) was employed for separation and quantification of the PFAS-compounds.

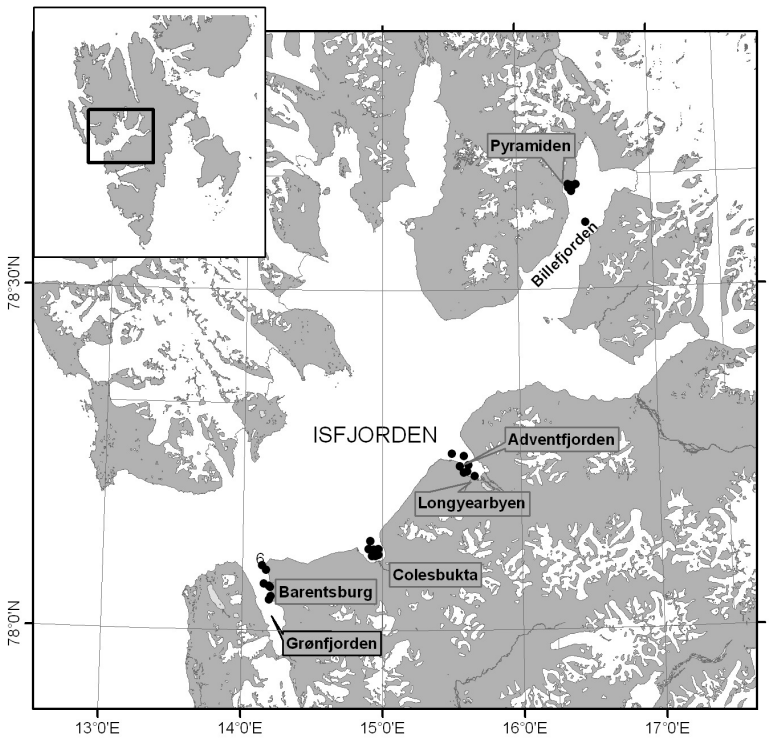

Figure 1. Map of Isfjorden, Svalbard, showing sampling stations with black circles. The sampling was carried out in September 2005.

3 Results and discussion

Sediment characteristics: On most stations the sediment was relatively fine grained (> 70 % < 63 µm) (Table 1). High concentrations of organic carbon (up to 275 mg/g) were measured on several stations in Grønfjorden (Table 1). The reason for this is probably discharges of sewage into the fjord, as well as dumping of excrements from domestic animals. Also in Adventfjorden TOC-levels were higher that the assumed background level for Svalbard fjords[4]. Also in Adventfjorden sewage from the settlement is discharged directly into the fjord. Low levels of organic carbon were measured in sediment collected outside the abandoned settlements in Billefjorden (Pyramiden) and Colesbukta.

Organochlorines: The highest PCB-levels were measured in Billefjorden (3.7 – 15.9 µg/kg dw), followed by Grønfjorden (0.9 – 8.5µg/kg dw), Adventfjorden (0.2 – 0.9 µg/kg dw) and Colesbukta (0.3 – 0.7 µg/kg dw) (Table 1). The PCB-levels outside Pyramiden and to a lesser extent outside Barentsburg have increased in recent years, as lower levels were measured on some of the same stations in 1998[4] . This may indicate that there still are active sources for PCBs in these areas.

The HCB-levels were generally low in the investigated fjords. However, slightly elevated levels were measured on some stations in all areas, except Colesbukta. The highest DDT-levels were measured outside the two Russian settlements; Barentsburg (0.8 – 7.0 µg/kg dw) and Pyramiden (0.6 – 1.2 µg/kg dw). Sediment from Adventfjorden had the lowest DDT-levels (0.1 – 0.4 µg/kg dw, Table 1). Generally DDT that has been long-range transported will be dominated by DDE, a stable metabolite of DDT. However, p,p-DDD and p,p-DDT were the dominant DDT-compounds in the sediment samples collected outside the Svalbard settlements, suggesting some past use of DDT on Svalbard.

Generally, the levels of all organochlorine contaminants included in the present study were higher than concentrations measured in open sea areas around Svalbard[5], but significantly lower than levels in harbours in mainland Norway[6, 7].

Table 1. Concentrations of PCBs, HCB and DDTs (µg/kg dw) in sediment from Isfjorden, Svalbard, September 2005.

Station	Area	Settlement	Grain size % < 63 µm	TOC (%)	Sum PCB* (µg/kg dw)	HCB (µg/kg dw)	Sum DDT (µg/kg dw)
LYB 1	Adventfjorden	Longyearbyen	35.97	0.89	0.46	0.09	0.09
LYB 2	Adventfjorden	Longyearbyen	94.28	2.07	0.19	0.27	0.09
LYB 3	Adventfjorden	Longyearbyen	97.20	3.44	0.85	0.24	0.22
LYB 4	Adventfjorden	Longyearbyen	85.05	2.14	0.88	0.55	0.35
14	Adventfjorden	Longyearbyen	98.75	2.27	0.61	0.31	0.15
15	Adventfjorden	Longyearbyen	96.62	2.07	0.63	0.33	0.17
16	Adventfjorden	Longyearbyen	92.77	1.71	0.66	0.43	0.19
BB 1	Grønfjorden	Barentsburg	86.29	4.06	8.53	0.50	6.95
BB 2	Grønfjorden	Barentsburg	28.24	16.50	2.83	0.21	3.63
BB 3	Grønfjorden	Barentsburg	42.17	1.42	6.72	0.26	1.02
5	Grønfjorden	Barentsburg	77.21	1.90	0.85	0.24	1.00
6	Grønfjorden	Barentsburg	74.74	1.49	1.65	0.50	0.76
7	Grønfjorden	Barentsburg	27.09	27.50	7.81	0.25	2.31
8	Grønfjorden	Barentsburg	93.94	1.86	2.60	0.56	0.87
PYR 1	Billefjorden	Pyramiden	98.95	0.65	15.90	0.09	1.20
PYR 2	Billefjorden	Pyramiden	97.33	0.64	13.20	0.12	0.98
PYR 3	Billefjorden	Pyramiden	94.36	0.76	8.91	0.21	1.02
PYR 4	Billefjorden	Pyramiden	94.74	0.90	6.44	0.21	1.05
4	Billefjorden	Pyramiden	94.78	0.70	4.62	0.57	0.72
10	Billefjorden	Pyramiden	96.87	0.78	6.64	0.13	1.12
11	Billefjorden	Pyramiden	95.32	1.26	3.73	0.21	0.57
CB 1	Colesbukta	Colesbukta	98.96	1.37	0.26	0.36	0.21
CB 3	Colesbukta	Colesbukta	96.98	1.35	0.70	0.36	0.34
CB 5	Colesbukta	Colesbukta	86.46	1.34	0.57	0.43	0.52

* Sum of CB 28, 52, 99, 101, 105, 118, 138, 180, 183, 187 and 194

PBDEs: Seven BDE-congeners (BDE 47, 99, 100, 153, 154, 183 and 209) were detected in one or more samples. The PBDE- concentrations were generally lower than the concentrations of PCB, DDT and HCB at the same stations (Table 1 and 2). The highest PBDE-concentration (1.1 µg/kg dw) was measured in sediment from Grønfjorden (station 7), at one of the stations with an exceptionally high TOC-concentration. BDE 209 was the dominant congener at 5 of the 8 stations that were analysed for PBDE, followed by BDE 47 and BDE 99. The concentration of BDE-209 was in the same range or even higher that levels measured in Norwegian harbours areas[8] .

Table 2. Concentrations of PBDEs and PFCs (µg/kg dw) in sediment from Isfjorden, Svalbard, September 2005.

Station	Location	Settlement	Sum PBDE* (µg/kg dw)	PFOS (µg/kg dw)	PFOA (µg/kg dw)	PFHxS (µg/kg dw)	PFNA (µg/kg dw)
LYB 1	Adventfjorden	Longyearbyen	0.25	0.10	0.16	< 0.01	0.14
14	Adventfjorden	Longyearbyen	0.05	0.25	< 0.11	< 0.01	< 0.11
16	Adventfjorden	Longyearbyen	0.25	0.31	0.12	< 0.01	< 0.11
5	Grønfjorden	Barentsburg	0.17	0.54	0.19	0.03	0.30
7	Grønfjorden	Barentsburg	1.10	0.11	< 0.11	< 0.01	< 0.11
10	Billefjorden	Pyramiden	0.40	0.28	< 0.11	< 0.01	< 0.11
11	Billefjorden	Pyramiden	0.11	0.41	0.44	0.02	0.15
CB 3	Colesbukta	Colesbukta	0.21	0.13	0.23	< 0.01	< 0.11

* sum of BDE 47, 99, 100, 138, 153, 154, 183 and 209

PFAS: The perfluorinated compounds (PFCs) were dominated by PFOS (Perfluorooctane sulfonate) (0.1 – 0.5 µg/kg dw) and PFOA (perfluorooctanoic acid) (< 0.1 – 0.4 µg/kg dw), but also PFHxS (perfluorohexane sulfonate) (< 0.01 – 0.03µg/kg dw) and PFNA (perfluorononanoic acid) (< 0.1 – 0.3 µg/kg dw) were detected in some of the samples. All other PFAS were below the detection limit. On most stations, sum PFCs were higher than sum PBDEs, but in the same range as sum DDT. There are few published data on levels of PFAS in sediment samples and the basis for comparison with other areas is therefore sparse. However, the presence of these compounds in areas that has been unpopulated for nearly 45 years (Colesbukta) confirm that they are long-range transported to Arctic areas.

Due to runoff from glaciers the sedimentation rate is high in the investigated fjords (Cochrane et al. 2001). A combination of high sedimentation rates and elevated levels of persistent organic compounds indicates that the fjord areas outside the main settlements on Svalbard are still receiving significant amounts of contaminants from local, as well as remote sources.

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