

# Lake-sediment evidence for local and remote sources of atmospherically deposited pollutants on Svalbard\*



N.L. Rose<sup>1</sup>, C.L. Rose<sup>2</sup>, J.F. Boyle<sup>3</sup> and P.G. Appleby<sup>4</sup>

<sup>1</sup> *Environmental Change Research Centre, University College London, 26 Bedford Way, London WC1H 0AP, U.K. (E-mail: nrose@geog.ucl.ac.uk)*

<sup>2</sup> *National Environmental Technology Centre, AEA Technology, Culham, Oxfordshire, OX14 3DB, U.K.*

<sup>3</sup> *Department of Geography, University of Liverpool, P.O. Box 147, Liverpool, L69 3BX, U.K. (E-mail: jfb@liverpool.ac.uk)*

<sup>4</sup> *Department of Mathematical Sciences, University of Liverpool, P.O. Box 147, Liverpool, L69 3BX, U.K. (E-mail: appleby@liverpool.ac.uk)*

Received 19 February 2001; accepted 23 November 2003

*Key words:* Atmospheric deposition, Arctic, PAH, PCB, Pollution, Spheroidal carbonaceous particles, Svalbard, Trace metals

\* This is the seventh in a series of nine papers published in this special issue dedicated to recent environmental change on Svalbard. H.J.B. Birks, Vivienne J. Jones, and Neil L. Rose were guest editors of this special issue.

## Abstract

Twenty-one lakes along the west coast of Svalbard were cored between 28 July and 14 August 1995. Five cores were  $^{210}\text{Pb}$  dated and analysed for spheroidal carbonaceous particles (SCPs), indicators of deposition from fossil-fuel combustion sources, and trace metals. Surface and pre-industrial levels of five cores were analysed for ten polychlorinated biphenyl (PCB) isomers and 16 polycyclic aromatic hydrocarbon (PAH) compounds, whilst all 21 surface sediments were analysed for SCPs. Temporal and spatial trends in the atmospheric deposition of pollutants were identified. Whilst temporal patterns of deposited pollutants may have been truncated due to concentrations falling below the limits of detection, spatial patterns showed elevated levels of SCP, PAH, PCB, and possibly Pb within 60 - 70 km of Isfjord.

Tenndammen (U), the closest site to Longyearbyen, showed the highest levels of contamination for all pollutants. Differences in the deposition patterns of PAH and PCB are thought to be due to local sources of PAH from coal combustion whilst PCB sources are remote. It is concluded that the impact from atmospheric deposition on Svalbard is due to a combination of spatially limited local sources superimposed on a broad-scale, long-range pattern.

## Introduction

The Svalbard archipelago lies between  $76^\circ$  and  $81^\circ\text{N}$  and  $10^\circ$  and  $30^\circ\text{E}$  (Figure 1). It is situated approximately half-way between the North Cape of Norway and the North Pole and is therefore far removed from major sources of atmospheric pollution. However, since the first reports of 'Arctic haze' by Mitchell (1956) studies have shown that significant long-range transport of atmospheric pollutants to Svalbard can occur and is thought to originate in the former Soviet Union, western Europe, and North America (e.g. Rahn and Shaw 1982; Pacyna and Ottar 1985; Pacyna et al. 1985; Barrie 1986; Heintzenberg 1989; Jaworowski 1989; Maenhaut et al. 1989; Grodzinska and Godzik 1991; Beine et al. 1996; Burkow and Kallenborn 2000). Data from the European Monitoring and Evaluation Programme (EMEP) (Berge 1997) suggest that attributable  $\text{SO}_x$  deposition on Svalbard (about one-third of the total  $\text{SO}_x$  deposition for annual mean data between 1985 - 1995) originates mainly from the Kola/Karelia region of Russia with other attributable inputs from the remainder of the Russian Federation, the UK, and marine sources.

Deposition of atmospheric pollutants on Svalbard has been attributed to long-range sources despite the presence of local mining industries since the turn of the century and coal-fired power stations in the Isfjord area (Longyearbyen, Barentsburg, and Pyramiden) for at least 40 years. Given the great distances from major sources in continental Europe or North America, these small, industrial point sources within Isfjord may combine to form a significant source of emission in this sensitive, low deposition area. Therefore, it may be that these local sources are not 'negligible' as has been suggested in previous studies (e.g. Lannefors et al. 1983) although their impact may be localised or their contribution to the total load difficult to define (Jaworowski 1989).

It has long been recognised that as well as providing a record of within-lake changes, lake sediments provide a reliable record of atmospheric deposition to the lake and its catchment. In areas with little or no historical records of contaminant deposition, sediment cores are often the only means by which long-term trends can be ascertained. To a lesser degree, and with caveats covering sedimentation-rate variability, contemporary lake surface-sediments have also been used to determine the spatial patterns of atmospheric deposition over a region.

This paper describes the temporal and spatial patterns of atmospherically deposited contaminants as recorded by a number of lake sediment cores taken from along the west coast of Svalbard in 1995. Comparison is made with additional sediment cores taken from similar sites in 1993. The analyses of these cores are used to identify the extent to which local and long-range sources are affecting the region.



Figure 1. Map showing sampling sites with respect to main settlements and local combustion sources. Inset, the location of Svalbard with respect to Fennoscandia and the North Pole.

## Methods

Twenty-one lakes along the west coast of Svalbard, between Bellsund (77° 33' N) and Albert I Land (79° 48' N), were sampled between 28 July and 14 August 1995. During this period field personnel lived and travelled aboard the boat 'Farm' from which an inflatable boat was used to carry equipment to the shore. This was then carried on foot to the lakes and hence most sites were within 1 km of the coast. The locations of the 21 sites (A - U) are shown in Figure 1 and are described in more detail in Birks et al. (2004).

Short sediment cores (ca. 20 cm) were taken from each site using a Glew (1989) gravity corer and extruded vertically in the field. At five sites, Ossian Sarsfjellet (C), Ytertjørna, (Q), Vassauga (S), Daltjørna (T) and Tenndammen (U), full sediment cores were extruded and stored whilst at the remainder surface sediments only were collected. For PAH and PCB analyses, the surface sediments (0-1 cm) of four cores were amalgamated, homogenised, and stored cool in hexane washed amber jars.

The five sediment cores were analysed for lithostratigraphy, trace metals (Boyle et al. 2004) and spheroidal carbonaceous particles (SCPs) and were dated radiometrically (Appleby 2004). Surface sediments from the remainder were analysed for SCPs. Surface and pre-industrial sediments were analysed for polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) at five sites.

Sediment cores from Arresjøen (Arsj), Birgervatnet (Bir), and 'Scurvy Pond' (Scur) in the north-west (Figure 1) were taken in 1993 using similar coring techniques. These cores

were also  $^{210}\text{Pb}$  dated and analysed for SCPs (Rose et al. 1999) and a range of persistent organic pollutants (Grimalt et al. in Wathne et al. 1995) as part of the EU funded project AL:PE 2.

### *Sediment dating*

Radiometric dates were obtained for the sediment cores by analysing for  $^{210}\text{Pb}$ ,  $^{226}\text{Ra}$ ,  $^{137}\text{Cs}$ , and  $^{241}\text{Am}$  by direct gamma assay using a well-type coaxial low background intrinsic germanium detector (Appleby et al. 1986). Details of the methods and individual chronologies of the sediment cores are discussed in Appleby (2004).

### *Spheroidal carbonaceous particles (SCPs)*

SCPs are produced from the high temperature combustion of fossil-fuels and have no natural sources. Therefore, in lake sediments they provide an unambiguous record of industrially-derived, atmospherically deposited pollution. Unlike some deposited pollutants (e.g. S, Cd, Zn), SCPs are inert to changes in water and sediment chemistry and consequently the SCP record is both reliable and robust. The particles are composed mainly of elemental carbon and hence are chemically resistant though physically fragile. Unwanted fractions of the sediment can therefore be removed by the use of strong mineral acids without affecting the particles.

The procedure for extraction and enumeration of SCPs from the Svalbard surface sediments and cores followed Rose (1994). Sequential attack using  $\text{HNO}_3$ , HF, and HCl removed organic, siliceous, and carbonate fractions, respectively, resulting in a suspension of mainly carbonaceous material in water. A known fraction of this suspension was then evaporated onto a coverslip and the number of SCPs counted at 400 times magnification under a light microscope. Sediment concentrations are calculated as 'number of SCPs per gram dry mass of sediment' or  $\text{g DM}^{-1}$ .

### *Trace metals*

Sample preparation and analysis followed the methods described in Boyle et al. (2004).

### *PCBs and PAHs*

PCB and PAH analyses followed the isotope dilution methods detailed in Rose (1996). Approximately 30 g of sample, air-dried at ambient temperature in a clean-air cabinet, was Soxhlet-extracted with hexane/acetone after the addition of a cocktail of internal standards,  $^{13}\text{C}$ -labelled PCBs, or deuterated PAHs, respectively. Measurement was achieved using a Hewlett Packard 5970 GC-MS equipped with a 50m DBS 0.2  $\mu\text{m}$  film capillary column. The mass spectrometer was operated in selective ion monitoring mode. Sixteen PAH compounds, listed by the World Health Organisation, were analysed. These were naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(ah,ac)anthracene, and benzo(ghi)perylene. The limit of detection was  $1 \text{ ng g}^{-1}$ . Total PAH ( $\Sigma\text{PAH}$ ) was estimated from the sum of the 16 compounds. PCBs 28, 52, 77, 101, 118, 126, 138, 153, 169, and 180 were analysed with total PCBs estimated using an extrapolated value derived from the total PCB levels (T3 to H7 total congeners) and the sum of the seven isomers. Analytical blanks for both PCBs and PAHs yielded values below the limits of detection.

Recoveries for all PCB compounds were >60% whilst recoveries for the PAHs varied from between 40 – 55% for the lightest compounds (naphthalene, acenaphthylene, acenaphthene, fluorene) to > 60% (the rest). Therefore, as the possibility of loss via volatilisation during air-drying is greatest for these lighter compounds, we have adopted the approach of Sanders et al. (1993) whereby the data for these lightest four PAH are not included further in our discussion.

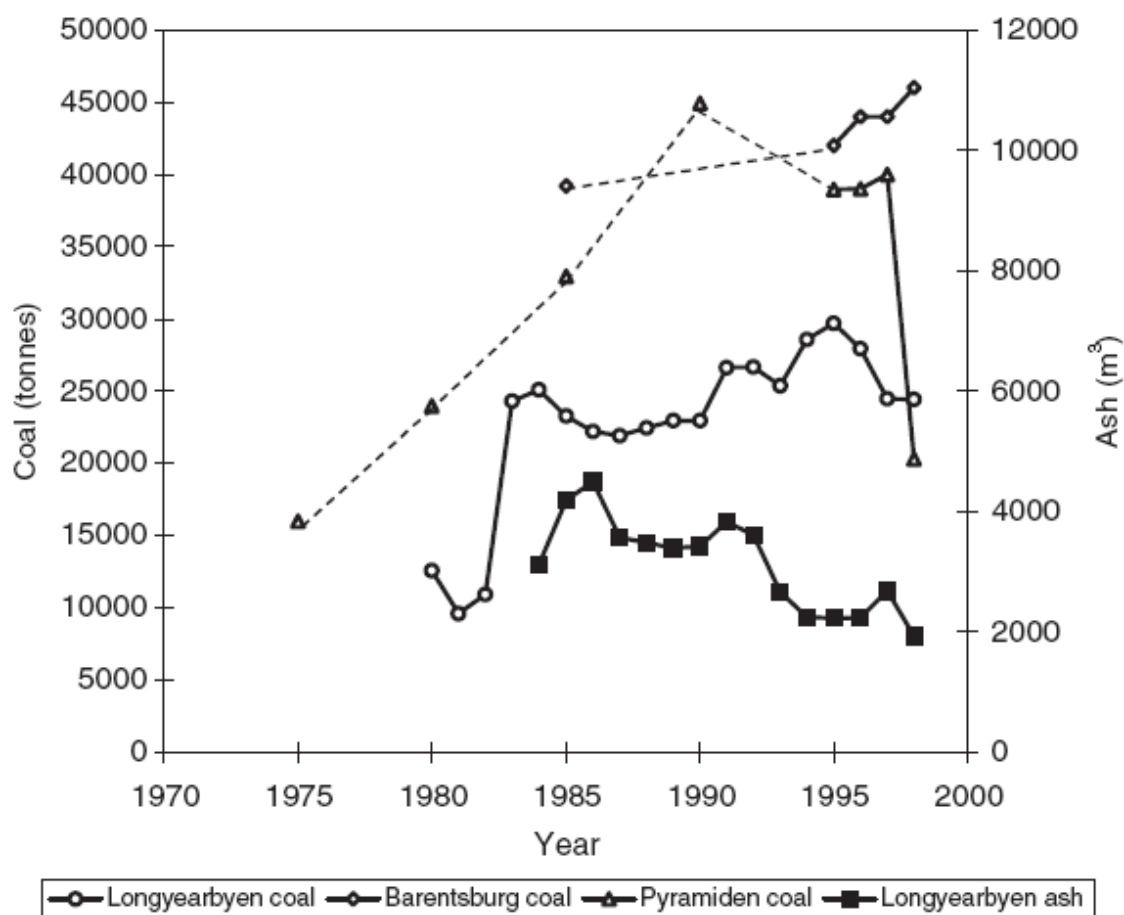


Figure 2. Annual coal combustion (tonnes) for the Longyearbyen, Pyramiden and Barentsburg power stations, and ash production (m<sup>3</sup>) for Longyearbyen power station.

### Local sources of contamination

Power production in Longyearbyen has always principally been based on coal combustion. However, the power plant in operation before 1983 also used considerable quantities of diesel for back-up generators (Kovacs 1996), although this has been reduced in the current power station and coal use has increased (O.J. Sylte, Svalbard Samfunnsdrift; pers. comm.) (Figure 2). Electricity demand and hence coal consumption (and ash production) show strong seasonal patterns (Figure 3) with almost 70% of consumption occurring in the period October to April (Statistics from Longyearbyen power station, pers. comm.). Similar seasonal trends have been observed at Zeppelinfjell, Ny-Ålesund in atmospheric concentrations of SO<sub>2</sub>-S, SO<sub>4</sub>-S (Jaworowski 1989), trace metals, and some organic species (Berg et al. 1996).

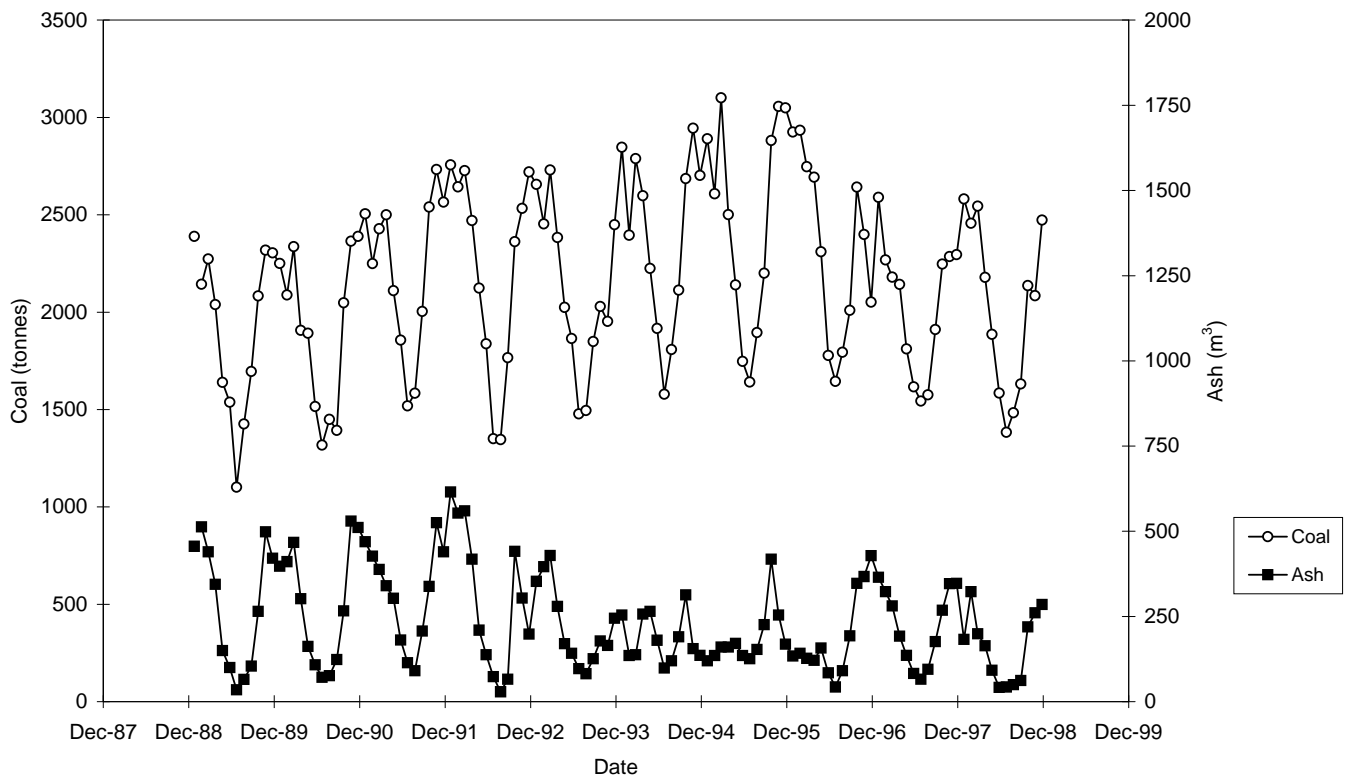


Figure 3. Monthly coal combustion (tonnes) and ash production ( $\text{m}^3$ ) for the Longyearbyen power station 1989-1998.

Svalbard does not fall under the State Pollution Authority (SFT) guidelines for power production, but although no emission standards are required, it is recommended that Norwegian settlements burn coal that is less than 2.5% sulphur by weight and that they do not produce more than 46 g of dust per hour. Coal used in the Longyearbyen plant falls below this sulphur level (B. Bjørnsen, Svalbard Samfunnsdrift A/S, pers. comm.) and a multicyclone rinsing system reduces particulate emissions (Brekke 1996). However, occasional releases of 'black smoke' occur irregularly during repair change-overs (Kovacs 1996). No transformers, containing PCB-bearing oil, are currently used in the plant. Data on previous PCB use were not available.

With the closure of all but a single mine in Longyearbyen, most coal production by Store Norske Spitsbergen Kulkompani (SNSK) is now concentrated in Svea on Van Mijenfjorden (Kovacs 1996). However, a coal-fired power generating station is considered too expensive given the power needs of the small town and hence there is no coal burning. Power is produced by three diesel generators although emissions have not been measured. At Ny-Ålesund, power production is by gas-oil powered generators and these have been identified as a source of local pollution in the area (Beine et al. 1996).

Until autumn 1998, power at Barentsburg was generated through the burning of its low sulphur coal. There were three large generators within the plant, two ran continuously whilst a third operated as a back-up. All domestic and industrial power for the town was generated at this one station and the plant was capable of an output of 60 – 70 MW. This plant was the largest coal consumer on Svalbard (Figure 2) and whilst there were no filters on the stacks, an air centrifugation process removed the largest of the particulates. Emissions were not monitored and all gases produced through coal combustion were emitted to the environment (Kovacs 1996). The situation was similar at the other main Russian settlement of Pyramiden. Power generation through the combustion of coal was undertaken from at least 1956. As at Barentsburg, the plant operated continuously and had a maximum capacity of 75 MW.

Emissions were not routinely monitored. Production at both Pyramiden and Barentsburg ceased in autumn 1998 (O. Krohn and M. Eggestad, Syssemlannen på Svalbard, pers. comm.).

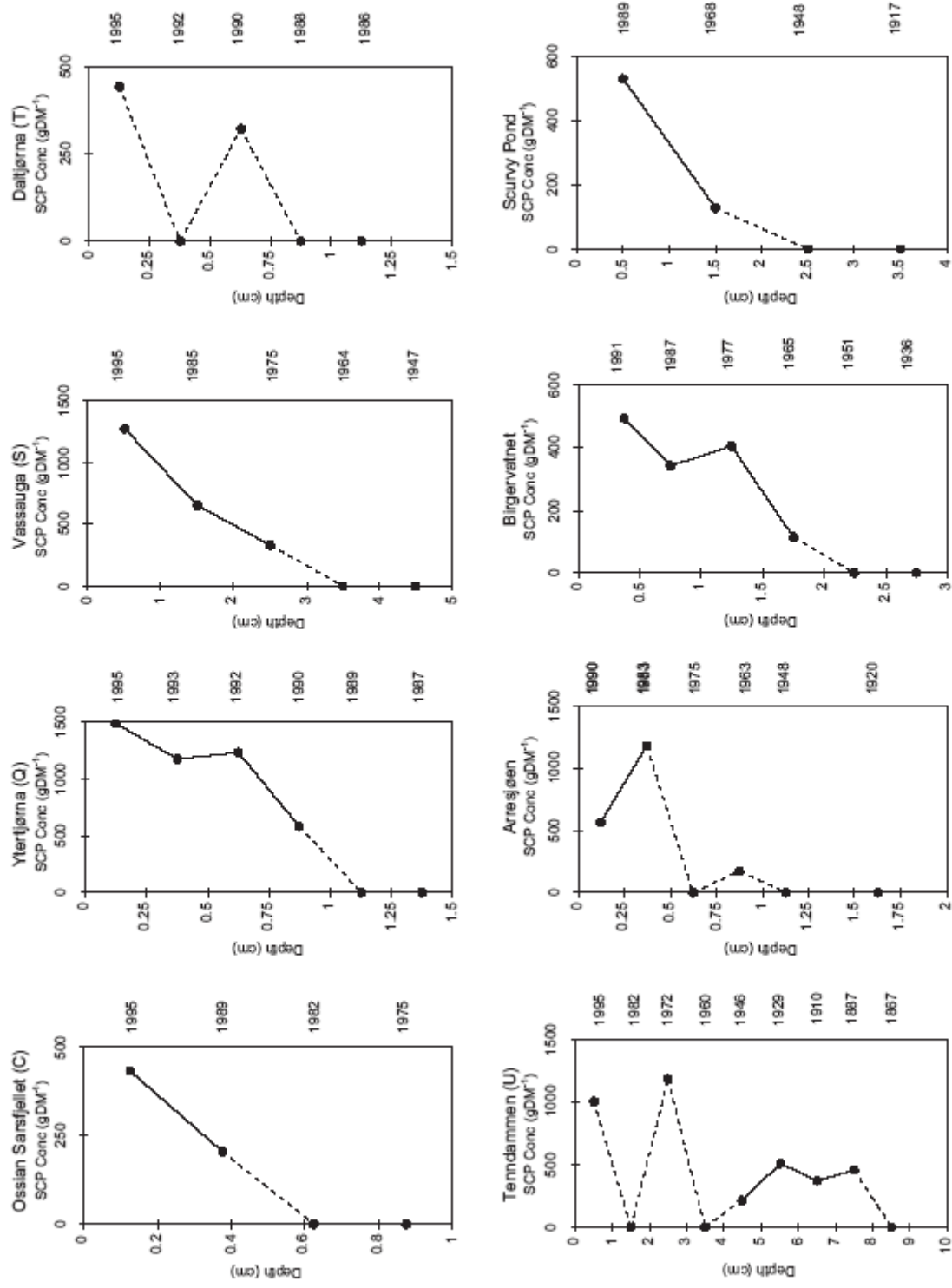


Figure 4. Historical profiles of SCP concentration (g DM<sup>-1</sup>) against sediment depth and <sup>210</sup>Pb dates for the eight analysed sediment cores. Solid lines connect SCP concentrations above detection limit. Dotted lines connect to concentrations below detection limit, here represented as 0 g DM<sup>-1</sup>.

## Results

### SCPs

The  $^{210}\text{Pb}$  dated SCP concentration profiles for the five analysed cores (and three 1993 cores) are shown in Figure 4. All sites show the presence of SCPs in the uppermost levels indicating a low but measurable contamination from fossil-fuel sources in recent times. The presence of SCPs in Ossian Sarsfjellet (C), Ytertjørna (Q), and Daltjørna (T) is only observed in post-1980 sediments. At Vassauga (S), Arresjøen (Arsj), Birgervatnet (Bir), and ‘Scurvy Pond’ (Scur) SCPs are present in post-1960 sediments, whilst only Tenndammen (U) shows a SCP presence over what might be considered a ‘full’ record post-1900. Therefore, it would appear that the SCP record in the other cores is truncated as a result of the detection limit of the technique rather than a lack of atmospheric deposition of these contaminants. This is also true of the presence of  $0 \text{ g DM}^{-1}$  values within the individual profiles. Whilst this means that interpretation of the profiles is limited, it does show that a significant increase in deposition occurred at the beginning of the 1980s sufficient to take the SCP record from below to above the detection limit. For this reason, it may be significant that the longer profiles (particularly lake U) are nearest to Isfjord and the local emission sources. In particular, coal consumption at the Longyearbyen power station shows a considerable increase in 1983 (Figure 2) when the former station was replaced (O.J. Sylte, Svalbard Samfunnsdrift; pers. comm.) and this may have been significant in elevating SCP concentrations above the detection limit at this time.

The spatial distribution of SCPs in the surface sediments of the 21 lakes is shown in Figure 5. The presence of SCPs was recorded in all sites except three, Trongdalen (F), Salatberget (N) and ‘Draba Pond’ (O). The locations of these lakes are unremarkable and, although they are in the northern half of the distribution, they do not form a geographical cluster, nor do they have any specific characteristics in common not shared by any other sites in the data-set (Birks et al. 2004). Therefore, because of the presence of SCPs in the surface sediments of adjacent lakes, the absence of SCPs is thought to be due to a concentration below the limit of detection (300, 150, and 200  $\text{g DM}^{-1}$ , respectively).

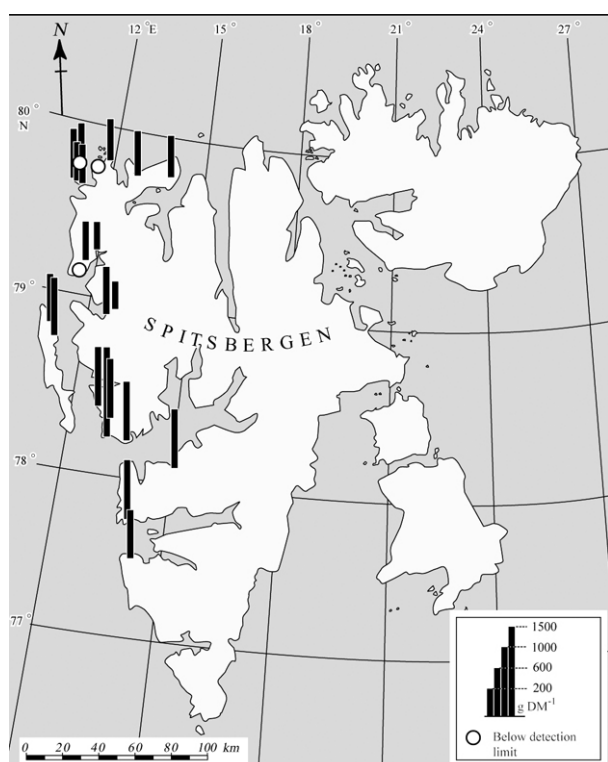


Figure 5. Surface sediment SCP concentrations (as number of particles per gram dry mass of sediment –  $\text{g DM}^{-1}$ ).



## Metals

The Pb concentration profiles for the five analysed cores (and Arresjøen core from 1993) are shown in Figure 6. Measured values are shown along with estimates of natural concentrations and indicate that at Ossian Sarsfjellet (C), Tenndammen (U), and Arresjøen (Arsj) measured values exceed natural estimates in recent sediments. For Ossian Sarsfjellet and Arresjøen this occurs in post-1970 sediments whilst at Tenndammen this exceedence can be observed from much earlier, in the late-19<sup>th</sup> or early 20<sup>th</sup> century. These data are thus broadly supportive of the SCP data.

## PAHs and PCBs

Selected PCB isomers and PAH compounds were determined in surface sediments and pre-industrial samples from five sites, Ossian Sarsfjellet (C), 'Bjørnvatnet' (I), Ytertjørna (Q), Daltjørna (T), and Tenndammen (U). These data are presented in Table 1. Data for the earlier sediment core from Arresjøen (Arsj) were obtained from Grimalt et al. (in Wathne et al. 1993).

PCB data are presented in Table 1. For surface samples, all concentrations are low but Tenndammen (U) shows the highest concentrations for all measured isomers. 'Bjørnvatnet' (I) and Ytertjørna (Q) show lower but similar concentrations for all isomers whilst Ossian Sarsfjellet (C) and Daltjørna (T) have the lowest surface-sediment concentrations. Arresjøen (Arsj) shows lower surface PCB concentrations than any of these sites ( $\Sigma\text{PCB} = 0.5 \text{ ng g}^{-1}$ ) and pre-industrial levels are below the limit of detection. With regard to surface enrichment (surface minus pre-industrial values), 'Bjørnvatnet' (I) and Ytertjørna (Q) show no enrichment, whilst the other sites show enrichments of between 0.5 and 2.57  $\text{ng g}^{-1}$ . Of these, Tenndammen (U) is the highest.

PAH data are given in Table 2. Surface concentrations are highest in Tenndammen (U) for all measured compounds. Concentrations are generally in the order  $U > Q > T > C \approx I$  and therefore appear to decrease with distance from Isfjord. However, the Arresjøen (Arsj) data confound this pattern showing surface PAH concentrations intermediate between Ytertjørna (Q) and Tenndammen (U). With regard to surface enrichment, only Ossian Sarsfjellet (C) and Arresjøen (Arsj) show a positive enrichment. All other sites have higher PAH concentrations in the pre-industrial sample than the surface sediment.

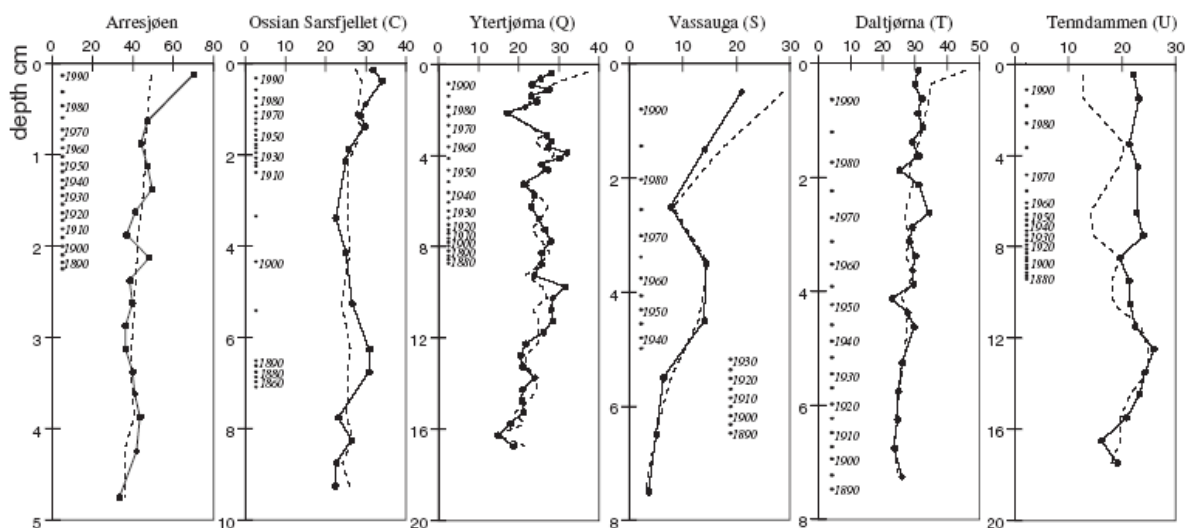


Figure 6. Lead concentration profiles. Measured values are shown as a solid line. The estimated natural concentration is shown as a dashed line.

Table 1. PCB data for surface and pre-industrial sediment samples. All values in ng g<sup>-1</sup>. nd = below the limit of detection (0.1 ng g<sup>-1</sup>).

Isomer	Ossian (C)		'Bjørnvatnet' (I)		Ytertjørna (Q)		Daltjørna (T)		Tenndammen (U)	
	Surface	Pre-industrial	Surface	Pre-industrial	Surface	Pre-industrial	Surface	Pre-industrial	Surface	Pre-industrial
28	0.27	0.42	0.84	0.83	0.83	0.81	0.30	0.15	1.24	0.84
52	0.43	0.30	1.05	1.05	0.95	1.91	0.31	0.22	1.80	1.82
77	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
101	0.77	0.50	1.92	1.49	1.13	2.91	0.58	0.28	3.23	3.54
118	0.25	0.13	0.55	0.49	0.77	0.88	0.18	0.12	1.45	0.89
126	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
138	0.36	0.16	0.82	0.88	1.08	1.26	0.36	0.15	2.24	1.36
153	0.53	0.27	1.22	1.28	1.27	1.89	0.63	0.23	2.88	2.15
169	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
180	0.13	nd	nd	0.48	0.41	0.41	0.22	0.10	0.68	0.35
Σ 10 isomers	2.74	1.78	6.40	6.50	6.44	10.07	2.58	1.25	13.52	10.95
Surface enrichment	0.96		-0.10		- 3.63		1.33		2.57	

## Discussion

### *Temporal distribution*

Interpretation of the SCP profiles presented in Figure 4 is limited as concentrations fall below the detection limit of the technique resulting in truncated records. In six of the eight cores, however, the maximum SCP concentration occurs in the surface sample indicating a maximum contamination from fossil-fuel combustion sources at the time of sampling i.e. the mid-1990s (early 1990s for Birgervatnet and 'Scurvy Pond'). This is in good agreement with local coal combustion data presented in Figure 2, where maximum total consumption of coal for the Isfjord power stations occurred in 1993. This suggests that there is an influence of local rather than remote sources on these sites as the European pattern for SCP profiles is usually one of a concentration maximum in the late-1970s (e.g. Rose et al. 1995).

The two sites for which the surface concentration is not the maximum, Tenndammen (U) and Arresjøen (Arsj), show maxima in 1972 and 1983, respectively. Interestingly, these are, respectively, the closest and one of the most remote sites from the Isfjord power stations indicating that these temporal patterns are not primarily determined by particle transport mechanisms. Data for the Longyearbyen power station (Figure 2) show that since the commissioning of the new station in 1983, ash production has decreased whilst coal consumption has increased. This suggests an increase in the influence of, or efficiency in, particle arrestor technology at the site and would explain a surface decline in SCP concentration, certainly at Tenndammen. However, if this is the case then it is currently unclear why this pattern is not observed at the other sites. Ironically, between the time of sampling and the writing of this paper, the power stations at both Barentsburg and Pyramiden have ceased operation. Therefore, if sampling resolution allowed, new sediment cores could now provide an even better opportunity of confirming the pattern of influence of these local stations.

Data from other studies also suggest that a decrease in contamination might be expected in recent years. Temporal trends of acidity and excess sulphate in ice cores taken from a number of areas on Svalbard (Simões and Zagorodnov 2001) show a maximum in the late-1970s with decreases in both parameters observed from the late-1980s onwards.

Similarly, a 58% decrease in the annual mean concentration of atmospheric SO<sub>2</sub> has also been reported between 1980 and 1995 (Tørseth 1996).

Table 2. PAH data for surface and pre-industrial sediment samples. All values in ng g<sup>-1</sup>. nd = below the limit of detection (1 ng g<sup>-1</sup>).

Compound	Ossian (C)		'Bjørnvatnet' (I)		Ytertjørna (Q)		Daltjørna (T)		Tenndammen (U)	
	Surface	Pre-industrial	Surface	Pre-industrial	Surface	Pre-industrial	Surface	Pre-industrial	Surface	Pre-industrial
Anthracene	nd	nd	nd	10	nd	39	4	nd	25	11
Fluoranthene	7	nd	15	10	14	182	14	31	54	56
Pyrene	3	nd	8	5	11	137	6	16	39	80
Benzo(a)anthracene	nd	nd	nd	nd	nd	3	nd	1	0	2
Chrysene	10	nd	nd	nd	11	62	13	29	29	84
Benzo(b)fluoranthene	nd	nd	nd	nd	1	144	nd	3	26	118
Benzo(k)fluoranthene	nd	nd	nd	nd	14	38	nd	nd	18	21
Benzo(a)pyrene	nd	nd	nd	nd	nd	31	nd	nd	nd	nd
Indenopyrene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Dibenzo(ah.ac)anthracene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Benzo(ghi)perylene	nd	nd	nd	nd	nd	nd	nd	nd	nd	7
Σ 11 compounds	20	nd	23	25	51	640	37	80	191	379
Surface enrichment	20		-2		-589		-43		-188	

As regards the historical record, Ossian Sarsfjellet (C), Ytertjørna (Q), and Daltjørna (T) first show a presence of SCPs in the late-1980s, Vassauga (S) in the mid-1970s, Arresjøen (Arsj), Birgervatnet (Bir), and 'Scurvy Pond' (Scur) in the 1960s, and Tenndammen (U) in the late-19<sup>th</sup> or early-20<sup>th</sup> century. This variability is undoubtedly due to the detection limit of the technique, although as already indicated, the commissioning of a new power station at Longyearbyen in 1983 may well have been influential in raising the SCP sediment concentrations at these sites above the detection limit for the first time.

The longer Tenndammen (U) profile shows some agreement with long-term coal production records and in the absence of consumption statistics these provide a helpful, although by no means totally robust, surrogate. Coal production began in the early years of the 20<sup>th</sup> century, at around the time the SCP record began, and a period of sustained production continued through to the Second World War when production temporarily ceased and the SCP record fell below the limit of detection. A rapid increase in production occurred between 1946 and 1955 with a peak in 1967, and the SCP peak is <sup>210</sup>Pb dated to have occurred a few years later. Since 1985 there has been a general decline in coal production whilst the Tenndammen SCP profile decreases from 1972 to the surface via another fall below the limit of detection. This longer history of contamination at the Tenndammen site is supported by the Pb data although testing for an anthropogenic signal in the Pb concentration profiles is critically dependent upon the baseline correction method. If baseline Pb is modelled on Ti (Figure 6), then an excess is found, which shows a similar depth profile to the SCP record. If the baseline is modelled on both Ti and organic matter, this excess disappears. The correlation of excess Pb with SCPs would seem to support the former. However, as argued by Boyle et al. (2004), this correlation could have arisen from mutual dilution effects. Therefore, it is possible to conclude that the profiles are compatible with an anthropogenic contamination signal, but the evidence is open to doubt. The full geochemical record is discussed in more detail in Boyle et al (2004).

The Arresjøen SCP profile also shows some temporal similarities with other contaminant species, but at this site it is the record of some sulphur-containing heterocyclics (S-PAH) such as benzo(b)naphthothiophenes and 4-methylbenzothiophene (Fernandez et al. 2002). This confirms a fossil-fuel combustion influence on atmospheric deposition at the site.

Concentrations of PCBs, HCB, and p,p'-DDE at Arresjøen are also low, but measurable back to ca. 1900 (Grimalt et al. in Wathne et al. 1995).

Little temporal interpretation is possible for the PCB and PAH data from our study as only surface and pre-industrial samples were analysed from five sites. These are further complicated by the elevated levels in the pre-industrial samples (Table 1). There are several possible reasons for this, suggested by Sanders et al (1992). First, small traces of PCBs and PAHs may have been transferred from recent sediments to deeper uncontaminated sediments by mixing, bioturbation, or sampling and extruding methods. Second, samples have been contaminated during preparation or analysis. Third, peaks appearing on the chromatogram matching the retention time of the PCB or PAH species may not be the species themselves, but a co-eluting species from the sample matrix. Fourth, there may be real pre-industrial levels in the environment. Although the third possibility cannot be totally discounted in this study, the first and second seem unlikely due to the good condition of the blanks, which were run in parallel with the samples (see Methods) and the well-resolved sediment profiles of other analysed contaminant species.

With regard to pre-industrial levels of PCBs, it is now thought that coplanar species are formed by *de novo* synthesis from particulate organic carbon (Boers et al. 1993; Schoonenboom et al. 1993) and therefore, it is possible that the presence of PCBs in pre-industrial sediments may represent pre-industrial levels of PCBs in the environment. However, it is unlikely that these would occur at greater levels than in recent times.

PAHs are produced from natural sources such as forest-fires and so their presence in pre-industrial samples is not unexpected. However, although it seems unlikely that these levels would be as high as recent industrial levels, considerable contamination could have been derived from atmospheric emissions as a result of whale blubber processing. Whaling was undertaken on a massive scale around Svalbard from the late-16<sup>th</sup> to early-17<sup>th</sup> centuries with ca. 50,000 bowhead whales being taken over this period by Dutch whaling companies alone (Mehlum 1990). English, French, Spanish, and Danish-Norwegian, as well as Dutch whaling companies all operated around Svalbard during this period, each establishing summer stations to extract oil from whale blubber by boiling (Kovacs 1996). One of the main areas for these operations was Smeerenburg ('Blubber Town') in the north-west of Svalbard (Figure 1), established in 1619 and with 150 men involved solely in processing throughout the 1630s and 1640s. Although work at Smeerenburg ceased in the 1660s, this intensive operation could have had a considerable impact on the local environment and other settlements on Svalbard are likely to have had a similar effect. The cores taken for the PAH and PCB analyses were not dated but the pre-industrial samples were certainly earlier than the base of the <sup>210</sup>Pb record (Appleby 2004) in each case. The sediment accumulation rates of parallel dated cores from these sites (Appleby 2004) suggest that these samples could have covered the intensive whaling period and this may be a contributing factor to the high PAH concentrations in the pre-industrial samples. Further investigation is required to confirm this.

### *Spatial distribution*

Those surface-sediment SCP concentrations which are above detection limits (Figure 5) appear to fall into two groups, a low concentration group (150 – 600 g DM<sup>-1</sup>) and a higher concentration group (950 – 1500 g DM<sup>-1</sup>). This latter group comprises Veslekupen (A), Farmhamna (B), Ytertjørna (Q), Spålen (R), Vassauga (S), and Tenndammen (U), the six sites closest to Isfjord and hence the local power station sources (Figure 1). This suggests an impact on the surrounding region by these power stations. However, only one site, Daltjørna (T), lies

further south than this ‘high’ concentration group and further sites are required to confirm the presence of a SCP concentration decline to the south. A further factor that must be considered is variability in sediment accumulation rate, because with low SCP concentrations slight differences in accumulation rate could alter SCP distribution patterns. Despite the similarity of the sampled lakes in many physical respects (size, depth, lack of catchment disturbance, etc.), variability in bird and other animal impacts (Birks et al. 2004), especially at sites such as these where nutrient inputs are otherwise low, is likely to lead to significantly increased productivity and hence increased sedimentation rate. This effect cannot be ignored. Fortunately, five of the lakes studied (C, Q, S, T, and U) were  $^{210}\text{Pb}$  dated (Appleby 2004) and, in addition, Arresjøen (Arsj), Birgervatnet (Bir), and ‘Scurvy Pond’ (Scur) (Figure 1) sampled in 1993 as part of the EU funded AL:PE 2 project, have been analysed for both  $^{210}\text{Pb}$  and SCP (Rose et al. 1999). This allows the calculation of SCP/ $^{210}\text{Pb}$  inventory ratios. This ratio provides a ‘pollution index’ for each site compensating for variations in sediment accumulation rate through time, as well as inwash from the catchment. In SCP terms this ratio allows the best inter-site comparison available and has been used to give a European picture of total industrial SCP deposition at mountain lake sites (Rose et al. 1999).

The SCP/ $^{210}\text{Pb}$  inventory ratios for the Svalbard sites are shown in Figure 7 against distance from Longyearbyen as a surrogate for proximity to the Isfjord power stations. The SCP/ $^{210}\text{Pb}$  ratio for Tenndammen (U) is 9,100 whilst that of Vassauga (S) is 2,400. The other cores, possibly truncated due to the SCP limit of detection, give inventory ratios of between 90 – 750 showing the relative contamination of Tenndammen and Vassauga over and above that which might be described as ‘typical’ for Svalbard. This provides further evidence for a local source of SCP, and, by inference, other contamination by fossil-fuel pollutants, within ca. 60 - 70 km of these local sources.

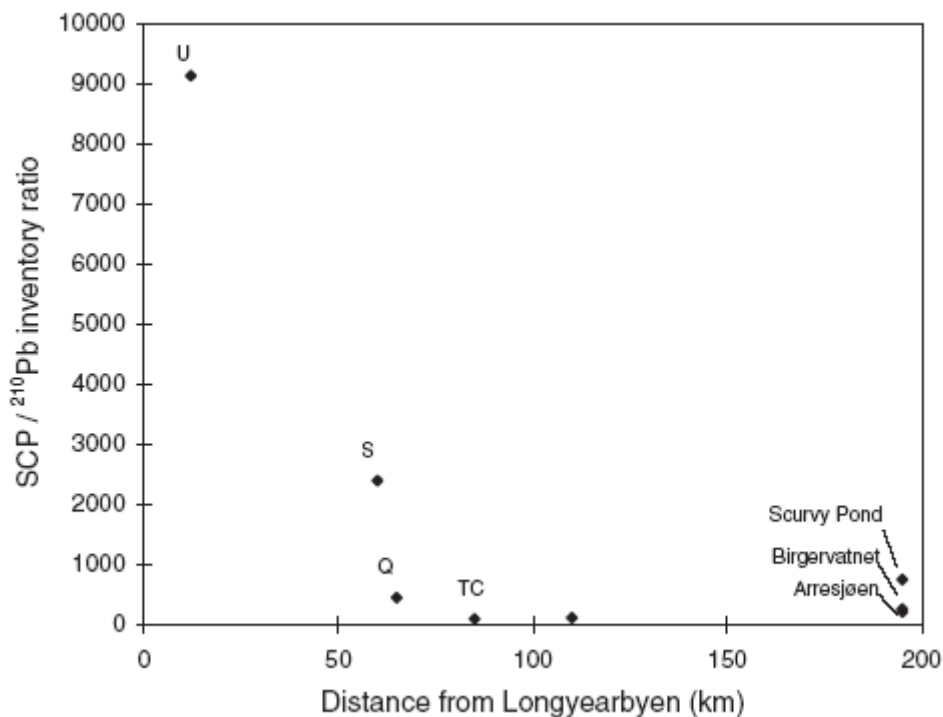


Figure 7. SCP/ $^{210}\text{Pb}$  inventory plotted against distance from Longyearbyen (as a surrogate for the power station sources in Isfjord)

Despite showing evidence for elevated levels of SCPs in the sediment record, by comparison with remote European mountain lakes, even Tenndammen (U) has only received moderate contamination over its post-industrial depositional history. Vassauga (S) shows comparable levels with the cleanest European mountain sites and the remainder of the Svalbard lakes show levels an order of magnitude lower. Lake sites such as Øvre Neådalsvatn in mid-Norway (used as the mountain lake reference site in the EU funded AL:PE and MOLAR projects) and Saanajärvi in Finnish Lapland, show SCP/<sup>210</sup>Pb inventory ratios of 1,870 and 1,350, respectively, whilst equally remote but slightly more contaminated AL:PE / MOLAR sites, such as the Spanish Pyrenean site Estany Redo and the Swiss site Jorisee, show ratios of 7,350 and 7,000, respectively (Rose and Appleby, unpublished data), equivalent to levels in Tenndammen. Other European mountain lake sites show higher levels of contamination. Starolesnienske Pleso and Nizne Terianske in the Slovakian Tatra mountains show SCP/<sup>210</sup>Pb inventory ratios of 11,700 and 14,000, respectively, Hagelsee in Switzerland has a ratio of 16,500 whilst that of Lochnagar in Scotland is over 40,000. Put in this context, even the elevated levels of contamination recorded by the Tenndammen sediments are quite low.

Similar spatial distributions are observed in surface sediments for the PAH and PCB data. Figure 8 shows the sum of the eleven PAH compounds and the ten PCB isomers as a function of distance from Longyearbyen. For PAHs there appears to be a decline in concentration with distance up to ca. 100 km, whilst for PCBs elevated levels in 'Bjørnvatnet' (I) suggest a limited influence beyond Ytertjørna (Q) of 60 – 70 km. However, it should be noted that these PCB and PAH data are concentrations rather than accumulation rates and therefore a slow sediment accumulation rate at 'Bjørnvatnet' could also explain elevated values at this site.

We therefore propose that the pattern of contamination in Svalbard surface sediments is one of local impact from the power stations in the Isfjord area super-imposed on a long-range signal from sources in Europe, Russia, and North America. From our data the influence of local sources is not observable at distances greater than ca. 60 - 70 km from Longyearbyen. Beyond this radius local and long-range impacts are not distinguishable.

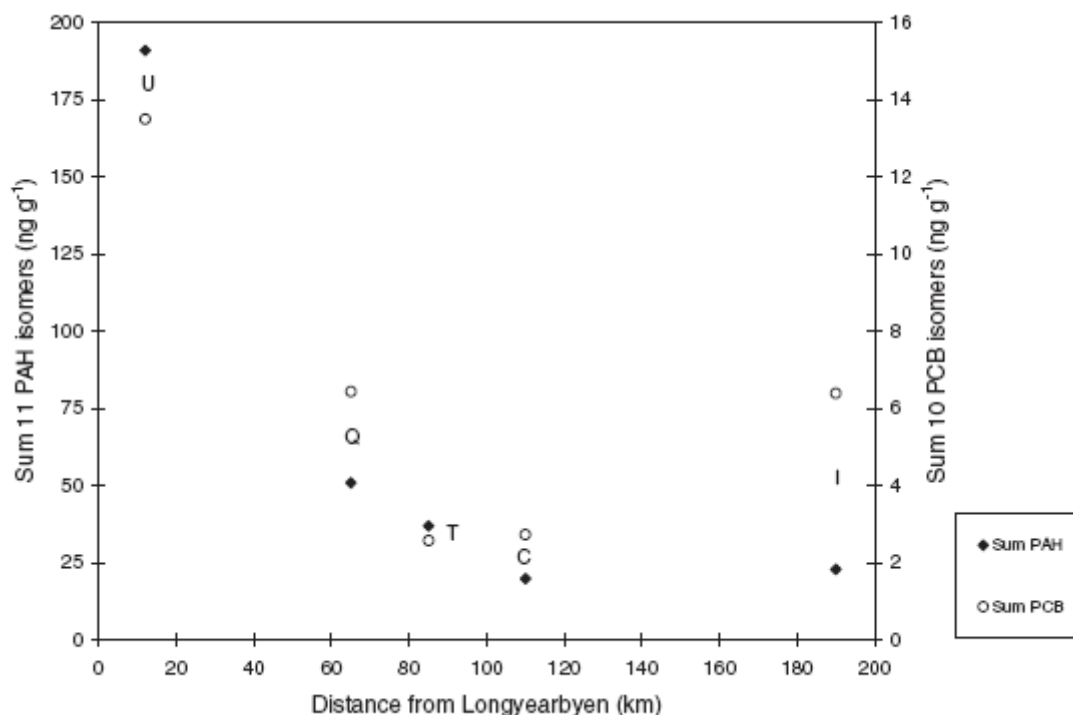


Figure 8. Sum of 11 PAH compounds and 10 PCB isomers plotted as distance from Longyearbyen.

#### Long-range versus local sources

The global fractionation effect should cause lighter semi-volatile species to become enriched with respect to heavier ones moving from lower latitudes towards the north (e.g. Wania and Mackay 1996). Therefore, lighter PAH and PCB species in the Svalbard lake sediments should be enriched over heavier species when compared with lake sites at lower latitudes and ratios of heavier to lighter species should decrease as latitude increases. Table 3 shows the ratios of PAH and PCB species (selected for data availability at the most sites) in the surface sediments of the five Svalbard lakes; Loch Coire nan Arr, a site in north-west Scotland (Rose and Rippey 2002); and two sites from the AL:PE European mountain lake data-set, Estany Redo in the Spanish Pyrenees and Schwarzsee ob Solden in the Austrian Alps (data from Grimalt et al. in Wathne et al. 1995).

Table 3. Ratios of heavy:light PCB and PAH species in European lake surface sediments at different latitudes. n/a = data not available.

Site	Estany Redo	Schwarzsee ob Solden	Loch Coire nan Arr	T	U	Q	C	I
Country	Spain	Austria	UK	Svalbard				
Latitude (N)	42°38'	47°52'	57°24'	77°34'	78°06'	78°14'	78°57'	79°40'
PCB153 : PCB28	8.2	n/a	5.3	2.1	2.3	1.5	1.9	1.4
Fluoranthene: Fluorene	38.0	12.8	7.5	3.5	1.9	1.6	1.2	1.0
Chrysene : Fluorene	n/a	n/a	8.9	3.3	1.0	1.2	1.7	n/a

Both PCB and PAH ratio data show decreases with latitude as predicted by the fractionation effect, and for the PCB153:PCB28 and fluoranthene:fluorene data this decrease also appears to be observable within the Svalbard data-set. However, the trends in this decrease for the two types of compound are quite different, with the PCB data showing a

linear decrease with latitude whilst the PAH data show an exponential decrease. Combustion of coal is a major source of PAH and hence the Isfjord power stations constitute a significant local source. Conversely, there are no industrial sources of PCB on Svalbard although it is now thought that emissions from coal combustion may contribute (Boers et al. 1993; Kocan et al. 1991). Therefore, one explanation for the difference in these trends is that the sources of PCBs are mainly from a location remote from Svalbard whilst the PAH trend is due to a combination of long-range transport from remote sources combined with a significant input from coal combustion on Svalbard itself. This conclusion is in agreement with the results from marine sediment work undertaken in 1997 (Olsson et al. 1998).

Further supporting evidence for this hypothesis comes from measurements of atmospheric trace contaminants at Zeppelinfjell, Ny-Ålesund (Berg et al. 1996). Annual patterns of trace elements (including arsenic, a trace element previously used as a coal indicator, e.g. Sadasivan and Negi 1990) and some PAH species show peak concentrations in the winter months, especially January and December, with low concentrations through the summer and therefore these parallel coal consumption patterns (Figure 3). Conversely, the trends in other organic contaminants not thought to be derived from fossil-fuel combustion (e.g. HCB, PCB species,  $\gamma$ -HCH) do not show this seasonal pattern and therefore the temporal PAH and metal trends are not merely due to factors such as meteorology. Hence, although there may be some influence from the gas-oil generators around Ny-Ålesund (Beine et al. 1996), metals and PAHs can be linked to Svalbard coal consumption, whilst PCBs and other non-combustion organics are from other, probably remote, sources.

## Conclusions

The power stations at Longyearbyen, Pyramidene, and Barentsburg burned 30,000, 34,000, and 42,000 tonnes of coal in 1995, respectively (Brekke 1996). In European industrial terms these quantities are small but when combined in this area, they represent a significant point source of emission. However, although these sources may account for elevated levels of contaminants within a radius of 60 - 70 km, the presence of lower but consistent levels of contamination in all sites beyond this area suggests a more diffuse long-range source. The patterns observed therefore suggest a small but measurable impact from the local sources in Isfjord superimposed on a long-range signal. The record of atmospheric deposition in the sediments is therefore most likely to be a combination of the two. With the closure of Pyramidene and Barentsburg in the autumn of 1998, it may be possible to test this hypothesis in the future as the impact of local sources is reduced. Once this is translated into the slowly accumulating sediment record then the patterns in SCP, PAH, and PCB should become more similar as local impact is lessened with respect to long-range transport.

Spatial data also allow an estimate of the area impacted by local deposition over and above any long-range or 'background' sources. Our data suggest that the distance at which local contamination from the Isfjord sources is observable above the background is 60 - 80 km and this represents a land area of 7,000 - 9,500 km<sup>2</sup> receiving enhanced deposition. This area of influence may be a minimum as Lien et al (1993) show critical load of acidity (S + N) exceedances not only to the north and south of the immediate Isfjord area, but also in the north-west (around Danskøya), in the north of Nordaustlandet, the eastern edge of Wijdefjorden, and in the south around Hornsund. However, in a European context, even the elevated levels of contamination recorded by the most contaminated Svalbard sediments are low and the question remains whether the small amounts of deposition described here are sufficient that a significant, measurable change in biota can be observed. Critical load of acidity exceedances (Lien et al. 1993) would suggest that this should be the case. Although



there is no diatom evidence for acidification at any of the sites in this current study (Jones and Birks 2004), there is some evidence from chrysophyte cysts (Betts-Piper et al. 2004) for acidification of several lakes in north-west Svalbard on Danskøya and near Krossfjorden.

### **Acknowledgements**

Funding for this study was obtained from Norges forskningsråd (grant number 107745/730), whilst funding for the earlier work on Arresjøen was funded by the EU under the AL:PE 2 programme (Contract No: EV5V-CT92-0205).

We thank John Birks, Nick Cox, Sharon Foster, Hans Lund, Don Monteith, Marianne Prytz, and John Sweeney for their help with the fieldwork and assistance on Svalbard. We are also grateful to Ole Ketil Bøkseth, Magny Eggestad, Ottar Krohn and Ann-Kristin Olsen of the Sysselmann's Office, Jon Roar Andersen, Kristjan Kristjansson, and Berit Kvæven of the Norwegian Pollution Control Authority for information, and to Jorunn Larsen and an anonymous reviewer for comments on the manuscript. Finally, we thank Alwyn Fernandes and Bernard Bushby at AEA Technology, Harwell, UK for the PAH and PCB analytical work, and the Cartographic Office, Department of Geography in University College London for producing the maps.

### **References**

- Appleby P.G. 2004. Recent environmental change and human impact in Svalbard: Sediment chronology. *J. Paleolim.* (this issue)
- Appleby P.G., Nolan P., Gifford D.W., Godfrey M.J., Oldfield F., Anderson N.J. and Battarbee R.W. 1986.  $^{210}\text{Pb}$  dating by low background gamma counting. *Hydrobiologia.* 141: 21-27.
- Barrie L.A. 1986. Arctic air pollution: An overview of current knowledge. *Atmos. Envir.* 20: 643-663.
- Beine H.J., Engardt M., Jaffe D.A., Hov Ø., Holmén K. and Stordal F. 1996. Measurements of NO<sub>x</sub> and aerosol particles at the Ny-Ålesund Zeppelin mountain station on Svalbard: Influence of regional and local pollution sources. *Atmos. Envir.* 30: 1067-1079.
- Berg T., Hjellbrekke A-G. and Skjelmoen J.E. 1996. Heavy metals and POPs within the ECE region. EMEP / CCC-Report 8/96. NILU, Kjeller, Norway, 187 pp.
- Berge E. (ed.) 1997. Transboundary air pollution in Europe. MSC-W Status report 1997. Part 2; Numerical Addendum to Emissions, dispersion and trends of acidifying and eutrophying agents. EMEP/MSW Report 1/97.
- Betts-Piper A.M., Zeeb B.A. and Smol J.P. 2004. Distribution and autecology of chrysophyte cysts from high arctic Svalbard lakes: preliminary evidence of recent environmental change. *J. Paleolim.* (this issue)
- Birks H.J.B., Monteith D.T., Rose N.L., Jones V.J. and Peglar S.M. 2004. Recent environmental change and atmospheric contamination on Svalbard as recorded by lake sediments – modern limnology, vegetation and pollen deposition. *J. Paleolim.* (this issue)
- Boers, J.P., De Leer E.W.B., Gramberg L. and De Koning L. 1993. Levels of co-planar PCBs in flue gases of high temperature processes and their occurrence in environmental samples. Short papers of the 13<sup>th</sup> International Symposium on chlorinated dioxins and related compounds, (Vienna, Austria. Sept. 1993) 11: 233-236.
- Boyle, J.F., Birks H.J.B., Rose N.L. and Appleby P.G. 2004. Recent environmental change and human impacts on Svalbard: the lake geochemical record. *J. Paleolim.* (this issue)

- Brekke, B. 1996. Discharges from human settlements on Svalbard. Norsk Polarinstitutt Report, 9 pp.
- Burkow, I.C and Kallenborn R. 2000. Sources and transport of persistent pollutants to the Arctic Toxicol. Lett. 112-113: 87-92.
- Fernández P., Rose N.L., Vilanova R.M. and Grimalt J.O. 2002. Spatial and temporal comparison of polycyclic aromatic hydrocarbons and spheroidal carbonaceous particles in remote European lakes. *Wat., Air Soil Pollut. FOCUS* 2: 261-274
- Glew J.R. 1989. A new trigger mechanism for sediment samplers. *J. Paleolim.* 2: 241-243.
- Grodzinska K. and Godzik B. 1991. Heavy metals and sulphur in mosses from southern Spitsbergen. *Polar Res.* 9: 133-140.
- Heintzenberg J. 1989. Arctic Haze: Air pollution in polar regions. *Ambio* 18: 50-55.
- Jaworowski Z. 1989. Pollution of the Norwegian Arctic: A review. Norsk Polarinstitutt. Rapport 55, Oslo.
- Jones V.J. and Birks H.J.B. 2004. Lake-sediment records of recent environmental change on Svalbard: results of diatom analysis. *J. Paleolim.* (this issue)
- Kocan A., Petrik J., Chovancová J., Neubauerova L. and Bezacinsky M. 1991. PCBs in the environment. *Chemistry in Britain*, May 1991, pp. 435-438.
- Kovacs K.M. 1996. The impact of human settlement on Svalbard. Contaminant risks to the environment. *Akvaplan - NIVA* 410.96.1043, 74 pp.
- Lannefors H., Heintzenberg J. and Hansson H. Ch. 1983. A comprehensive study of physical and chemical parameters of the Arctic summer aerosol; results from the Swedish expedition Ymer-80. *Tellus* 35B: 40-54.
- Lien L., Henriksen A. and Traaen T.S. 1993. Critical loads of acidity to surface waters – Svalbard. *NIVA report O-90102*, 19 pp.
- Maenhaut W., Cornille P., Pacyna J.M. and Vitols V. 1989. Trace element composition and origin of the atmospheric aerosol in the Norwegian Arctic. *Atmos. Envir.* 23: 2551 – 2569.
- Mehlum F. 1990. Birds and mammals of Svalbard. Norsk Polarinstitutt, Oslo, 140 pp.
- Mitchell M. 1956. Visual range in the polar regions with particular reference to the Alaskan Arctic. *J. Atmos. Terr. Phys. Special Suppl*: 195-211.
- Olsson, K., Savinov V., Gulliksen B. and Dahle S. 1998. Contaminants in marine sediments, Svalbard 1997. *Akvaplan-niva report* 414.98.1396, 36 pp.
- Pacyna J.M. and Ottar B. 1985. Transport and chemical composition of the summer aerosol in the Norwegian Arctic. *Atmos. Envir.* 19: 2109-2120.
- Pacyna J.M., Ottar B., Tomza U. and Maenhaut W. 1985. Long-range transport of trace elements to Ny-Ålesund, Spitsbergen. *Atmos. Envir.* 19: 857-865.
- Rahn K.A. and Shaw G.E. 1982. Sources and transport of Arctic pollution aerosols: A chronicle of six years of ONR research. *Naval Res. Rev.* March, S2-26.
- Rose C.L. 1996. PCBs and PAHs in Svalbard lake sediment cores. *AEA Technology National Environmental Technology Centre Report AEA/WMES/RCEC/18352007/Issue1*, 26 pp.
- Rose N.L. 1994. A note on further refinements to a procedure for the extraction of carbonaceous fly-ash particles from sediments. *J. Paleolim.* 11: 201 - 204.
- Rose N.L. and Rippey B. 2002. The historical record of PAH, PCB, trace metal and fly-ash particle deposition at a remote lake in north-west Scotland. *Envir. Pollut.* 117: 121 – 132.
- Rose N.L., Harlock S. and Appleby P.G. 1999. The spatial and temporal distributions of spheroidal carbonaceous fly-ash particles (SCP) in the sediment records of European mountain lakes. *Wat. Air Soil Pollut.* 113: 1-32.

- Rose N.L., Harlock S., Appleby P.G. and Battarbee R.W. 1995. Dating of recent lake sediments in the United Kingdom and Ireland using spheroidal carbonaceous particle (SCP) concentration profiles. *The Holocene*. 5: 328-335.
- Sadasivan S. and Negi B.S. 1990. Elemental characterization of atmospheric aerosols. *Sci. Tot. Envir.* 90: 269-279.
- Sanders G., Jones K.C., Hamilton-Taylor J. and Dörr H. 1992. Historical inputs of polychlorinated biphenyls and other organochlorines to a dated lacustrine sediment core in rural England. *Envir. Sci. Technicol.* 26: 394-396.
- Sanders G., Jones K.C., Hamilton-Taylor J. and Dorr H. 1993. Concentrations and deposition fluxes of polynuclear aromatic hydrocarbons and heavy metals in the dated sediments of a rural English lake. *Envir. Toxicol. Chem.* 12: 1567-1581.
- Schoonenboom M.H., Tromp P.C. and Olie K. 1993. The formation of co-planar PCBs, PCDDs and PCDFs in a fly-ash model system. Short papers of the 13<sup>th</sup> International Symposium on chlorinated dioxins and related compounds. Vienna, Austria, September 1993, 11: 277-280.
- Simões J.C. and Zagorodnov V.S. 2001. The record of anthropogenic pollution in snow and ice in Svalbard, Norway. *Atmos. Envir.* 35: 403-413.
- Tørseth, K. 1996. Overvåking av langtransportert forurenset luft og nedbør. Atmosfærisk tilførsel, 1995. NILU report OR 38/96, 189 pp.
- Wania F. and Mackay D. 1996. A global distribution model for persistent organic chemicals. *Sci. Tot. Envir.* 160/161: 211-232
- Wathne B., Patrick S.T. and Cameron N.G. (eds.) 1995. AL:PE - Acidification of mountain lakes: Palaeolimnology and ecology. Part 2 - Remote mountain lakes as indicators of air pollution and climate change. Report to the Commission of the European Communities, Research Council of Norway and the Austrian Research Foundation. NIVA Report No. 3638-97, 525 pp.