Tellus (1983), *35B*, 131–141

Seasonal variations of Cd, Pb, Cu and Ni levels in snow from the eastern Arctic Ocean

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(Manuscript received April 5; in final form September 13, 1982)

ABSTRACT

During the Swedish Arctic expedition "Ymer 80" into the area from North Greenland to Franz-Josef-Land in late summer 1980, freshly fallen snow, and snow from the previous fall/winter season were collected from ice floes. Lead, cadmium and copper analysis was performed on board ship, using the advanced voltammetric determination method of differential pulse anodic stripping voltammetry at rotating glassy carbon electrodes. The analytic operations were performed under a clean bench in a clean room container. Nickel, and tentatively, cobalt levels were analyzed in our home laboratory by differential pulse voltammetry after preconcentration by chelate adsorption at a hanging mercury drop electrode. Results from freshly fallen snow compared to snow from the previous season show that there exists a strong seasonal variation in trace metal deposition, indicating that pollution of the Arctic atmosphere is clearly limited to winter time, when atmospheric conditions favour long-distance transport of polluted air masses from Europe to the Arctic. Unexpectedly low mean levels of 0.4 ng kg^{-1} Cd, 13 ng kg^{-1} Pb, 20 ng kg^{-1} Cu and 22 ng kg^{-1} Ni were found in freshly fallen snow, levels that represent about 1/10 to 1/20 of those in annual condensed layers.

1. Introduction

During recent decades, increasing atmospheric pollution has given rise to concern that the natural cycles of the northern hemisphere may be seriously affected, due to a concentration of 90% of the total anthropogenic emissions in certain regions of this part of the globe. Anthropogenic sources are concentrated in central Europe and North America. Heavy metals like Cd, Pb, Cu and Ni, mainly bound to particles, are emitted into the atmosphere by heavy industry, coal burning, metallurgical plants and smelters, and nowadays also by garbage incineration (Nriagu, 1979; Lantzy and Mackenzie, 1979; Settle and Patterson, 1980; Schladot and Nürnberg, 1982). The combustion of petrol with added Pb-alkyls as antiknock agents in automobile traffic is a very significant source and an efficient means of introducing Pb-aerosols into the atmosphere. A large part of the metals emitted is deposited in close vicinity to the respective sources by dry or wet deposition, the latter being the most effective for the washout of heavy metals (Nguyen et al., 1979). Depending on the meteorological situation, fine particles, however, can be advected from the planetary boundary layer to the upper troposphere where they become involved in long-range transport (Fisher, 1978; Barrie et al., 1981; Borys and Rahn, 1981; Carlson, 1981; Heidam, 1981; Ottar, 1981; Rahn, 1981a,b; Shaw, 1981).

The second leg of the Swedish "Ymer-80" expedition from August 8 to September 20 to the Arctic offered unique possibilities for the study of trace metals such as Cd, Pb, Cu, Ni and Co in atmospheric depositions in this remote region in areas never before touched by man. Several of these trace metals are among the so-called "anomalously enriched elements" which exhibit high crustal enrichments in present-day tropospheric aerosols in remote areas in both hemispheres (Duce et al., 1975). These studies are not only desirable in order to complete global baselines, but are also of particular interest with respect to the

meteorological and geochemical features of the study area itself. The Arctic has its own specific regional character concerning meteorological conditions. It represents a more-or-less particle and metal source-free area, mainly out of reach of the prevailing midlatitude westerlies. However, it is situated in rather close proximity to the intensely industrialized Central Europe, Scandinavia and North America (Barrie et al., 1981; Carlson, 1981; Rahn, 1981a,b).

Annual mean values of trace metals in snow and ice layers have been determined by several groups (Murozumi et al., 1969; Weiss, 1975; Herron et al., 1977; Weiss et al., 1978; Boutron, 1979a, b; Davidson et al., 1981; Ng and Patterson, 1981) mainly in the area of Greenland, revealing a distinct, increasing lead pollution since the beginning of industrialization in Europe (Murozumi et al., 1969). It has been claimed by Rahn and McCaffrey (1979) that there are compositional differences in trace metal levels between Arctic aerosols and snow, but the work of Davidson et al. (1981) yielded no clear differences, at least in the composition of low-altitude aerosols compared to fresh and old snow. Trace metals in Arctic haze particles have been investigated and distinct seasonal variations have been detected (Barrie et al., 1981; Heintzenberg et al., 1981). Comparable seasonal variations should also be found in snow deposits, which has been proved by Davidson et al. (1981). Difficulties arise in detecting them in accumulated annual snow layers, as seasonal stratification has been blurred by snow drift. The second leg of the "Ymer-80" expedition in mid-August was expected to take place during a time of minimal long-distance transfer of atmospheric pollution to the Eastern Arctic ocean. The first snow in late summer as well as agglomerated snow samples from the previous fall and winter season could be collected, enabling the study of seasonal variations in trace metal content.

2. Experimental

2.1. *Cleaning procedures*

The careful preparations before an expedition include as a step of key significance the scrupulous cleaning of sampling bottles and other items for sample processing. The need for these prerequisites has been pointed out mainly by Patterson and Settle (1976), but their significance has been frequently underestimated. Detailed cleaning procedures have been described elsewhere (Mart, 1979) and only a short summary is given here.

Sample bottles made of conventional polyethylene are degreased with detergents. Acid-leach at about 70 °C, 4 days, with reagent-grade HCl, diluted 1:10. Repeat operation with new acid. Acid-leach another 4 days with high-purity HCl, diluted 1:20 with ultrapure water. Repeat this operation under dust-free conditions. Fill bottles with ultrapure water acidified to pH 2 and wrap them in 2 acid-leached conventional polyethylene bags for storage until use. These manipulations are effected under clean conditions, wearing polyethylene gloves and working under a clean bench. Conventional polyethylene bags are soaked in diluted acid baths, first reagent grade then ultrapure, diluted 1:20.

Teflon (TFE) is a sintered material; its cleaning needs a much longer time. Teflon-ware, like voltammetric cells and teflon shovels, is processed following a similar procedure to that described above. Degrease. Acid-leach at 70 °C, one week, with reagent-grade HNO_3, diluted 1:1 and repeat with fresh acid; repeat operation with ultrapure acid 1:10 and ultrapure water for at least one week at 90 °C.

2.2. *Sampling procedures*

2.2.1. *Collection of snow samples.* Special care was devoted to the collection of snow, as it is well-known, that in general, contamination encountered in the field severely plagues the accuracy of trace metal studies in snow and water. An example of the difficulties encountered is given in Table 1. During a heavy snowfall, collection of snow has been tried on board of "Ymer" using a large funnel as the sampling area. Collection of the same freshly

Table 1. *Snow sampled during cruise on board "Ymer" in comparison to snow collected on an ice floe; obvious contamination during collection on the research ship*

Sampling site*	Cd (ng kg^{-1})	Pb (ng kg^{-1})	Cu (ng kg^{-1})
"Ymer"	3	380	400
Ice floe	0.3	13	15

* Position: 81°43′ N 03°31′ W.

fallen snow from a virgin ice floe at 200 m distance from the ship demonstrated that it is extremely difficult to choose a place on board a ship for reliable collection of rain or snow.

Optimal sampling conditions were found when snow was falling during sampling, or when snowfall had occurred only a few hours earlier. Temperatures frequently were close to or below zero and wind strength was low, so that there was no wind drift. The upper layer of snow could be collected as freshly fallen virgin snow. The relevance of such samples could be proved by repeating snow collection at each sampling station.

Difficulties arose in collecting relevant snow samples that had fallen some days previously, that had wind-drifted and possibly been mixed with older snow layers having a higher trace metal content. A distinct stratification within a few cm snow depth could be found, depending on the fate of the drifted snow and on sunshine intensity and duration, causing melting of the snow surface. This is reflected clearly in the results in Table 3.

Nevertheless, this kind of drifted or freshly fallen snow was rather easy to collect. On each of our sampling stations, several samples were generally collected within an area of 100 × 100 m. Carefully precleaned widemouth polyethylene 0.5 l bottles were used. Bottles of this size are easy to clean and, above all, easy to handle in field missions. Until use, the bottles were wrapped in 2 polyethylene bags, the inner one having been precleaned to avoid contamination of the bottle during storage prior to use.

The collection procedure is as follows. Sampling is always effected upwind, filling the bottle by moving it in quarter circle movements through the upper layer of snow. After each filling movement, the operator proceeds 50 cm upwind, moving the bottle through only virgin snow layers. Contamination of the snow surface by the operator can thus be avoided by using this procedure and by the wearing of protective clothes by the operator, i.e. long plastic gloves and, as far as possible, clean room suits.

Snow to a depth up to 10 cm was collected after trimming back an area of about 1 m^2 with a teflon shovel proceeding into the wind direction for trimming and going upwind for snow collection according to the procedure described above.

Snow and harsh from the previous year were collected as far as possible in the same way, the mouth of the plastic bottle generally being hard enough for scrubbing. A specially designed ice axe of stainless steel and previously leached with acid was used for frozen and agglomerated snow layers. As could be proved by comparative analysis, the stainless steel tool gave no measurable blanks for Cd and Pb in snow collection.

2.3. *Analytical methods*

2.3.1. *Analysis on board and in home laboratory.* The trace metals Cd, Pb and Cu were determined simultaneously in one run by differential pulse anodic stripping voltammetry (DPASV) at rotating mercury film electrodes plated in situ on a glassy carbon substrate (MFE). Molten snow samples were in general analyzed within one day after collection. All samples were acidified to pH 2–3 by the addition of 1 ml hydrochloric acid, Suprapur® Merck, Darmstadt, to a 1 l sample. The samples that could not be measured at once, as samples for checks, were stored deep frozen at −20 °C until analysis at the home lab. As has been found previously, trace metal leaching from dust particles with weak acids is very effective (Nguyen et al., 1979). Trace metals in molten snow samples acidified to pH 2 represent about 90% of the total trace metal content.

A short summary of the analytical procedure will be given here. Three important steps have to be mentioned.

(i) *Preparation of working electrode.* Polish glassy carbon surface with 0.3 μ aluminium oxide and rinse carefully.

(ii) *Contamination check.* Run a contamination test with ultrapure water, pH 2, adjusted to 1 p.p.m. of Hg $(NO_3)_2$ and deoxygenated with high-purity N_2 for 10 min. Plate at −1 V for 6 min, and scan anodically, using the differential pulse mode. Trace metal levels, mainly Pb, roughly evaluated after a calibration curve, should correspond to the blanks of the ultrapure water used (see Section 2.5).

(iii) *Analysis of a sample.* If the electrode system has turned out to be clean (which is the case in 95% of such tests), replace test cell by a cell filled with the sample (around 50 g) previously outgassed and adjusted to 1 p.p.m. of $Hg(NO_3)_2$. The Hg film plated during the contamination check has not (!) been wiped off. Further outgassing for 2 min. Plate at −1 V for 6–30 min (longer plating time for levels below 1 ng kg^{-1}). Scan. First standard addition.

Second cathodic deposition for half the first plating time (3–15 min). Scan. Second standard addition, followed by third plating for one third of the first time (2–10 min). Scan. After analysis, the precise weight of the sample is determined. For evaluation of results, peaks are normalized to one common deposition time by using a programmable calculator.

The advantages of this procedure, such as saving analysis time and gaining accuracy, have been extensively described elsewhere (Mart et al., 1980; Mart, 1982; Mart et al., 1982). The main advantage of this voltammetric method, apart from its high sensitivity and inherent accuracy (Nürnberg, 1979), is that it could be used even under icebreaking conditions on board "Ymer".

2.3.2. *Analysis in home laboratory.* Samples of snow were also analyzed for their Ni-, and tentatively, for their Co-content. Usually Co was below the detection limit of 5 ng kg^{-1}. The voltammetric method used has been developed recently (Pihlar et al., 1981). In this approach, both metals are preconcentrated at the hanging mercury drop electrode surface by adsorption of their dimethylglyoxime chelates from an analyte adjusted to pH 9 with ammonia buffer. Subsequently the adsorbed chelates are reduced by application of differential pulse voltammetry.

2.4. *Apparatus*

Polarographs. PAR 174 A, EG & G Princeton Applied Research, Princeton N.J. The polarographs have been modified to achieve a higher sensitivity as described in detail elsewhere (Valenta et al., 1977).

Recorder. A *y–t* recorder, BD8 Kipp & Zonen, Delft, Netherlands, was used on board the "Ymer". In our home laboratory, a multichannel *y–t* recorder, model 2041 from Linseis, Selb, Germany, is connected to 2 polarographs for running 2 analyses in parallel.

Electrodes. On board ship, 2 rotating glassy carbon electrodes of our own construction could be connected to a polarograph. Alternatively, one of the electrodes was used for preparative purposes like polishing or outgassing of a sample, whilst the other one was connected to the polarograph for analysis. Details of the working electrodes, as well as of our home-made reference and counter electrodes, have been published elsewhere (Mart et al., 1980).

A hanging mercury drop electrode, model EA 290/2, Metrohm, Herisau, Switzerland, was used for the determination of Ni and Co.

2.5. *Blanks*

Ultraclean water and reagents. A Milli-RO-unit, Millipore Corp., Bedford, Massachusetts, U.S.A., was fed by tap water, which had been distilled from sea water on board "Ymer". Water supplied by this Milli-RO system was fed to a Milli-Q system. In our home laboratory, a Milli-Q system is fed directly with deionized water, yielding pure water of comparable quality. Trace metal blanks of this pure water depend on the life-span and obviously also on the charge of the ion exchange cartridges. Ni and Co levels in this water are below the blanks of the reagents used for their analysis, being 5 ng kg^{-1} and 1 ng kg^{-1} for Ni and Co, respectively. Trace metals in hydrochloric acid (Suprapur® Merck, Darmstadt) are guaranteed by the manufacturer to be below 5 p.p.b. In fact the level of the only important contaminant in this acid, Pb, has been determined to be about 200 ng kg^{-1}, thus giving a blank of 0.2 ng kg^{-1} in the sample (1 ml of acid added to a 1000 ml sample). Blanks from other trace metals as well as blanks stemming from the Hg-nitrate could only be evaluated as being below 0.1 ng kg^{-1}.

Trace metal leaching by acidified samples from the wall of polyethylene bottles stored at room temperature, has only been noticed for Pb with about 1 ng kg^{-1} per 2 to 3 weeks. These blanks can be avoided by cooling the bottles during longer storage. After the sampling procedure, a check of the polyethylene bag and the outer surface of the sampling bottle by leaching them with 25 ml of acidified pure water (pH 1) yielded absolute amounts of Pb below 2 ng.

Dust-controlled operations. On board ship, the electrochemical system was placed under a clean bench, class 100, with horizontal laminar air flow, installed into a clean room container. In our home laboratory, a laminar flow box with a vertical air pattern is used for controlled dust-free working. Requirements in the laboratory itself outside the clean bench area are then considerably less stringent; they correspond to class 10,000. Details have been described elsewhere (Mart, 1982).

2.6. *Analytical precision and accuracy*

Using confidence limits of 95%, the overall

analytical precision, including sampling and the few preparative steps like acidification, is better than 10% for all trace metals down to 10 ng kg^{-1}. Below 1 ng kg^{-1}, the relative standard deviation increases to 40% for Cd and Pb. Accuracy has been confirmed by intercomparative ultratrace analysis of deep sea water with Patterson and Bruland (Mart et al., 1980) and further intercomparison of sea water samples for Cd and Pb with Danielsson (unpublished results).

3. Results and discussion

The locations of the sampling stations during the second leg of the "Ymer-80" expedition are depicted in Fig. 1.

The low temperatures of the Arctic limit the moisture-bearing capacity of the air. Annual snow accumulations have been determined in Greenland by previous authors. At Dye-3, in southern Greenland, 46 g cm^{-2} yr^{-1} have been measured by Weiss et al. (1975). At station Centrale, in Central Greenland, 34 g cm^{-2} yr^{-1} have been reported by Boutron (1979a). The snowfall mainly occurs during late summer and fall. One year old snow, that could be collected during "Ymer 80" had its origin northeast of Greenland. It was transported southwards with the ice floes by the east Greenland current. Taking into account their medium life-span of 2 to 4 years, no distinct stratification over more than 2 years could be expected. Thus the main goal was a seasonal comparison of one year old snow and fresh snow. The first snowfall was registrated in mid-August and the last one occurred in mid-September, before leaving the area. Unfortunately, meteorological information for the air-mass trajectory calculations is rather limited in this area. Only short-range data could be used for a rough estimation of wind direction and possible origin of air masses.

In Table 2, fresh snow data are presented. Most of the data from each station fit into a narrow range. Analytical data of several days old snow (Table 3) are more random, as wind drift has mixed fresh and aged snow masses. Nevertheless, a distinct trend to low trace metal levels can be observed. But, as the fate and degree of mixing with older snow having higher trace metal levels is unknown, these results cannot be used for further extrapolation of seasonal variations.

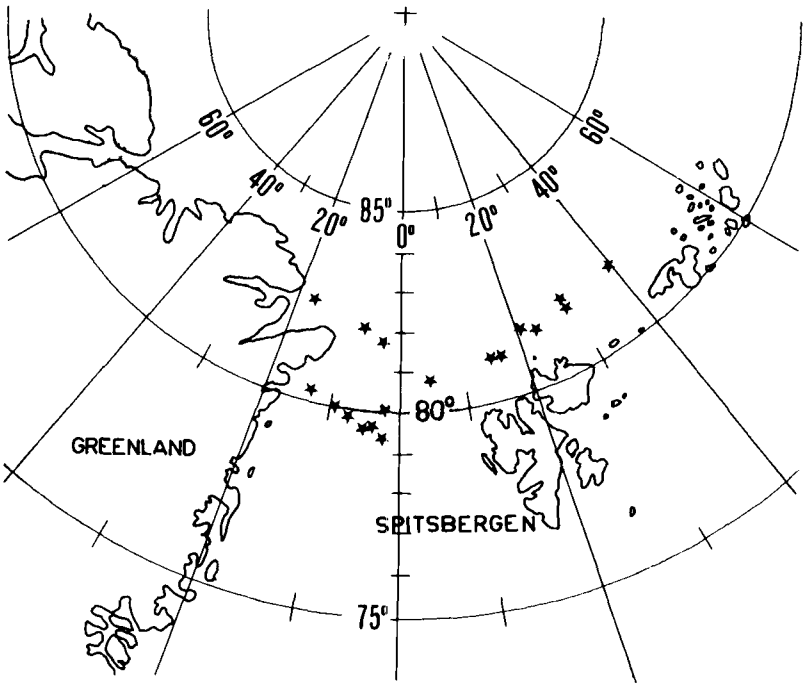

Fig. 1. Snow sampling stations during second leg of "Ymer-80" expedition from August 8 to September 20, 1980.

Table 2. *Freshly fallen virgin snow*

		Cd (ng kg^{-1})	Pb (ng kg^{-1})	Cu (ng kg^{-1})	Ni (ng kg^{-1})	Co (ng kg^{-1})
79°34′ N 04°43′ W		—	—	—	13	<5
August 27, 1980		0.5	16.0	15	—	—
		0.6	20.1	25	—	—
	$\bar{x}$	0.55	18.0	20	—	—
79°48′ N 07°10′ W		0.3	10.0	—	26	—
August 28, 1980		0.4	17.5	—	20	—
	$\bar{x}$	0.35	13.8	—	23	—
79°53′ N 09°20′ W		0.4	10.3	—	20	—
August 28, 1980						
80°14′ N 13°01′ W		0.4	12.5	10	22	⩽5
August 28, 1980		0.3	11.0	10	—	⩽5
		0.2	8.2	10	—	⩽5
		0.3	10.8	10	—	⩽5
		—	—	—	16	⩽5
	$\bar{x}$	0.3	10.6	10	19	—
	s	0.08	1.8	—	4.2	—
81°43′ N 03°31′ W		0.3	12.8	10	—	—
September 2, 1980		0.4	12.5	10	18	⩽5
		0.3	13.0	15	23	—
		0.3	11.6	15	19	—
		—	—	—	18	—
	$\bar{x}$	0.3	12.5	—	19.5	—
	s	0.05	0.6	—	2.4	—
80°47′ N 05°08′ E		0.4	14	—	32	—
September 5, 1980		0.5	16	—	22	—
	$\bar{x}$	0.45	15	—	27	—
80°00′ N 02°31′ W		0.3	11.4	20	—	—
September 6, 1980		0.3	12.3	15	23	—
		0.3	13.0	10	25	—
		0.4	18.1	15	—	—
		—	—	—	40	—
	$\bar{x}$	0.3	13.7	—	29	—
	s	0.05	3.0	—	9	—

A striking feature is the extremely low results in freshly fallen snow in Table 2 compared to data from snow of the previous season listed in Table 4. Table 5a shows a comparison of our data from condensed one-year-old snow layers with snow data of other authors obtained in previous years in Greenland. As can be noticed, our mean values fit well into the range found by other workers. In Table 5b results of trace metals in fresh snow published by Davidson et al. (1981) show a trend of seasonal variations, when the lower values of Cd and Pb are taken into consideration. But these variations are less pronounced and less distinct.

Taking into consideration the fact that most of the annual snowfall in the Arctic basin is associated with late summer and fall frontal cyclones, the fresh snow collected during the end of the "Ymer-80" expedition can be expected to represent about $\frac{1}{3}$ of the total snow covering. From this quantitative evaluation and from the results in freshly fallen snow, as well as from mean values in one-year-old snow, the fall/winter 79/80 snow data can be extrapolated. They are listed in Table 6.

A distinct winter pollution with a ratio fall/winter 79/80 to late summer 80 of 10–21 can be derived. This existence of a seasonal pollution in

Table 3. *Snow, a few days old*

	Trace metals (ng kg^{-1})					
	Cd	Pb	Cu	Ni	Co	Sampling depth (cm)
79°30′ N 04°05′ W	1.9	20	—	—	—	2
August 27, 1980	2.2	32	—	—	—	2
	2.8	29	—	44	—	2
	5.0*	180*	—	—	—	5*
79°17′ N 02°29′ W	3.1	28	—	—	—	2
August 27, 1980	3.7	43	25	101	—	2
	3.8	35	21	—	—	2
82°01′ N 07°06′ W	2.0	44	—	—	—	2
September 1, 1980	2.5	38	—	—	—	2
	2.0	37	—	27	6	2
81°27′ N 23°24′ E	1.0	34	—	69	⩽5	10†
September 11, 1980						
81°44′ N 29°47′ E	3.0	74	—	—	—	10†
September 13, 1980	0.5	14.8	—	—	—	20†
	3.2	48	48	—	—	30†
81°27′ N 29°21′ E	2.5	40	—	82	—	2
September 14, 1980						
81°53′ N 39°12′ E	—	—	40	35	8	2
September 18, 1980						

* Beginning of snow layers from last year.
† Accumulated drift snow.

Table 4. *Snow from last season 79/80*

		Cd (ng kg^{-1})	Pb (ng kg^{-1})	Cu (ng kg^{-1})	Ni (ng kg^{-1})	Co (ng kg^{-1})
82°24′ N 16°22′ W		5.2	196	80	180	6.0
		4.5	180	100	250	6.0
		6.0	180	110	160	—
	$\bar{x}$	5.2	185	97	197	6.0
81°37′ N 20°28′ E		4.0	177	—	185	—
		6.0	173	115	—	—
	$\bar{x}$	5.0	175	—	—	—
80°59′ N 14°52′ E		6.0	180	79	—	—
		1.6	226	—	205	—
	$\bar{x}$	3.8	203	—	—	—
81°00′ N 16°05′ E		5.2	338*	120	—	—

* Frozen harsh sample probably contaminated during sampling.
— Dashes indicate where analyses were not performed, mainly because of too small volumes of collected snow.

the Arctic extends the documented airborne pollution transport in the lower atmosphere during certain seasons to ranges of several thousand kilometers, because the Arctic region itself is a practically source-free area.

Although atmospheric data do not necessarily

Table 5a. *Comparison with published data: accumulated old snow*

Author	Origin	Year*	Mean value or range (ng kg^{-1}) Cd	Pb	Cu	Ni
Murozumi et al. (1969)	Greenland	1965	—	200	—	
Weiss et al. (1978)	Greenland	1965	3	—	—	
Herron et al. (1977)	Greenland	71/73	3	145–221	34–102	
Boutron (1979)	Greenland	73/74	0.7–85	128–899		
Davidson et al. (1981)	Greenland	78/79	11–<19	120–140	28–40	<49–<180
This work	area Greenland–Spitsbergen	1979	2.6–6	173–226	80–120	160–250

* Probable year of snowfall, which does not necessarily correspond to year of collection.

Table 5b. *Comparison with published data: fresh snow*

Author	Origin	Year*	Range (ng kg^{-1}) Cd	Pb	Cu	Ni
Davidson et al. (1981)	Greenland	78/79	7.8–17	42–150	35–65	51–<230
This work	area Greenland–Spitsbergen	1980	0.2–0.6	8–20	10–25	13–40

* Year of snowfall.

Table 6. *Comparison of snow data from the Arctic sea*

	Fresh snow late summer 1980 (ng kg^{-1})	Season 79/80 mean value (ng kg^{-1})	Extrapolated data fall/winter 79/80 (ng kg^{-1})	Extrapolated ratio fall/winter 79/80 / summer 80
Cd	0.4	5	7	17
range	0.2–0.6	1.6–6.0		
Pb	13	190	275	21
range	8–20	173–226		
Cu	13	97	130	10
range	10–25	80–120		
Ni	22	195	280	13
range	13–40	160–250		
Co	⩽5	6	⩽7	—

The extrapolated data for fall-winter season 79/80 are based on the assumption that the fresh snow collected represents $\frac{1}{3}$ of the total snow covering.

correlate with wet deposition data. Table 7 shows that comparable ratios winter-to-summer have been found by Heintzenberg et al. (1981). Atmospheric samples of late winter from Spitsbergen and late summer samples from N. Greenland, both areas of comparable geographic latitude, yield winter-to-summer ratios of 9 to 24. These findings are consistent with the general meteorological pattern that has been proposed by Rahn (1981a) and described by Kerr (1979). During summer, the Arctic is decoupled or cut off from the midlatitude pollution sources, whilst in winter the polar front lies south of the source areas. Rahn speculates that airborne pollutants originating in Europe can be

Table 7. *Average chemical composition of atmospheric aerosol samples*

	Late winter Ny Ålesund Spitsbergen air* (ng m^{-3})	Late summer Greenland Greenland air* (ng m^{-3})	Ratio $\frac{\text{winter}}{\text{summer}}$ air* (ng m^{-3})	Extrapolated ratio fall-winter 79/80 / summer 80 snow (ng kg^{-1})
Ni	0.7	0.08	9	13
Cu	1.9	—	—	10
Zn	3.2	0.18	18	—
Pb	4.9	0.20	24	20
Cd	—	—	—	17

* Taken from Heintzenberg et al. (1981).

In the 2 last columns, the ratios of air samples taken in winter and summer are compared with extrapolated ratios of fall/winter 79/80 to summer 80 snow samples.

Table 8. *Comparison of tropospheric fall-out fluxes in remote, source-free regions*

Site	Fall-out flux (ng cm^{-2} yr^{-1}) Cd	Pb	Cu
North Greenland, Camp Century (Murozumi et al., 1969)	—	8.8	—
Central Greenland, Centrale (Boutron, 1979)	0.37	7.8	1.9
Area Greenland–Spitsbergen This work*	0.15	6	2.91
Samoa (Patterson, unpublished results)	—	8	—
Central North-East Pacific (Schaule and Patterson, 1981)	—	60	—
Antarctic Dome C (Boutron, 1979)	0.02	0.1	0.1

* Snowfall data had to be derived from the Greenland results of other authors.

transferred over Scandinavia, causing acid rain, and further to the Arctic, and can even go across the North Pole to Alaska. The fact is, that this pathway is only open during winter time when meteorological conditions allow this long-range transport from European pollution sources into the Arctic.

Our data from the area Spitsbergen-Greenland suggest the existence of a transport of atmospheric metal pollution in the form of a well-aged continental aerosol. It has been shown that a considerable amount, particularly of the larger suspended particles, are sedimented or washed out by rain and snow within a range of typically 10 km from the respective emission sources (Nürnberg et al., 1982; Schladot and Nürnberg, 1982). However, small particles and aerosol which ascend from the planetary boundary layer into the upper troposphere obviously have a good chance of long-distance transport.

At Barrow, Alaska, distinct seasonal variations in excess sulfate and excess vanadium are reported, showing minimum values in August and September and a maximum in winter (Kerr, 1979). Vanadium originating from combustion of heavy oil is a good tracer for checking anthropogenic influences on atmospheric aerosols. Although the exact trajectory of the pollutants found in Alaska seems to vary from season to season and their origin in Europe remains speculative, there is obviously no doubt that pollution in the area from Greenland over Spitsbergen to Franz-Josef-Land originates in Europe. Recent research by Heintzenberg (private communication) leads to a simpler model. Trajectory analysis shows that polluted air masses can travel straight south–north, in contrast to the model of Rahn and McCaffrey (1979), which proposes a quasi half-circle path from Europe over Russia to the Arctic.

Tropospheric fall-out fluxes F, calculated from the relation $F = C \cdot A$, with C the mean of trace metal concentration in snow, and A the annual snow accumulation (evaluated after the findings of other authors in the Greenland area), are listed in Table 8. The data demonstrate that Antarctica is by far the cleanest region on earth. This is partially related to the fact that most of the anthropogenic emissions including heavy metals, occur in the

northern hemisphere. Antarctica is rather distant from the nearest potential source, compared to the Arctic which is located near to the North American continent and Europe. The 50° S circumpolar atmospheric convergence as well as the elevation of the Antarctic continent constitute an effective barrier against pollution. However, although less protected, the Arctic, as an area out of reach of the prevailing westerlies, seems to be subjected to comparably low deposition by tropospheric fall-out fluxes during summer.

An annual mean ratio (Pb Arctic snow)/(Pb Antarctic snow) of 65 is found by Boutron (1979b). A monthly mean ratio must be sensibly lower during late summer, as trace metal levels in snow will be present to the same order of magnitude if compared with the available data from Antarctica (Murozumi et al., 1969; Boutron and Lorius, 1979; Boutron, 1979b) This clearly reflects a rather effective protection of the Arctic by the polar front during summer. A further conclusion can be deduced from the low trace metal levels in late summer snow in the Arctic. Taking into account that Antarctica must be the cleanest area of the globe, trace metal levels should be lower there than the late summer results of the Arctic, e.g. below 5 ng kg^{-1} for Pb and below 1 ng kg^{-1} for Cd. Future research will reveal that a number of hitherto published data from Antarctic samples must be affected by contamination during sampling.

4. Acknowledgements

The author thanks the Royal Swedish Academy of Sciences for the opportunity to participate in the second leg of the "Ymer-80" expedition. He is greatly indebted to L. G. Danielsson, Department of Analytical and Marine Chemistry, Chalmers Institute of Technology and University of Gothenburg, Sweden, for his careful preparation of the clean room container on board of the "Ymer" and for valuable cooperation, and to H. C. Hansson, Lund Institute of Technology, Sweden, for his support in sampling. Manifold technical support by captain and crew of the "Ymer" is gratefully acknowledged. The author also expresses his thanks to H. W. Nürnberg for stimulating discussions and for a critical reading of the manuscript.

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