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Deposition of atmospheric trace metals in northern Sweden as measured in the snowpack

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ABSTRACT

In late February and early March, 1984, the snowpack of northern Scandinavia, with emphasis on northern Sweden, was sampled and analyzed for trace metals (Cd, Cu, Fe, Mn, Pb and Zn) and major ions. A comparison of major ion concentrations in the snowpack and monthly precipitation samples indicates that little of the major ions have escaped from the snowpack. Presumably, this is also true for trace metals. Metal concentrations in the region decrease from the Baltic coast towards the Swedish interior. The lowest metal concentrations are found in the Swedish mountains near the Norwegian border. Concentrations in this area are comparable to concentrations found in snow in Greenland and the Euopean Arctic near Spitsbergen. The concentration of Cd, Pb, Zn and sulfate in the snowpack are highly correlated to one another, and it is concluded that the deposition of these metals in northern Sweden during winter months is due mainly to long-range transport.

1. Introduction

Since trace metals have the potential to adversely affect man and the environment, interest has grown in monitoring their atmospheric deposition. In Sweden, a national survey of metal concentrations in mosses is performed every 5 years to assess any temporal or spatial changes in metal deposition (Rühling and Tyler, 1984). In recent years, it has been observed that large-scale decreases of trace metal deposition has occurred. This decrease has been related to known changes in trace metal atmospheric emissions in Sweden and Europe. Moss studies are useful in assessing temporal and relative spatial differences in trace metal input, but do not provide information on the absolute magnitude of atmospheric deposition. Therefore, the routine monitoring of trace metals in atmospheric precipitation was begun in Sweden in 1983. Currently, atmospheric precipitation is collected on a monthly basis in bulk collectors at 6 locations (Ross, 1984).

As demonstrated by Wright and Dovland (1978), Belikova et al. (1984) and Barrie and Vet (1984), regional snowpack surveys are valuable tools in assessing the deposition of atmospheric pollutants during winter months in high latitudes. If the sampling period is in late winter, snowpack surveys also provide information on the input of atmospheric pollutants to the biosphere during the spring snow melt. The sudden surge of acidic components and temporary acidification of lakes and streams during spring is well-documented in both Canada and Scandinavia (National Research Council of Canada, 1981; Swedish Ministry of Agriculture Environment '82 Committee, 1982).

Measurements of atmospheric pollution deposition by chemical analysis of the snowpack is suitable in regions where the snow remains on the ground for several months at sub-zero temperatures. This allows for a long enough sampling time to smooth out storm-to-storm variations. When attempting to make estimates of the atmospheric deposition of soluble ions, one must take into account the movement and possible leaching of ions from the snowpack by meltwater during winter thaws (Johannessen and Henriksson, 1978). To evaluate such losses, the snowpack can be sampled

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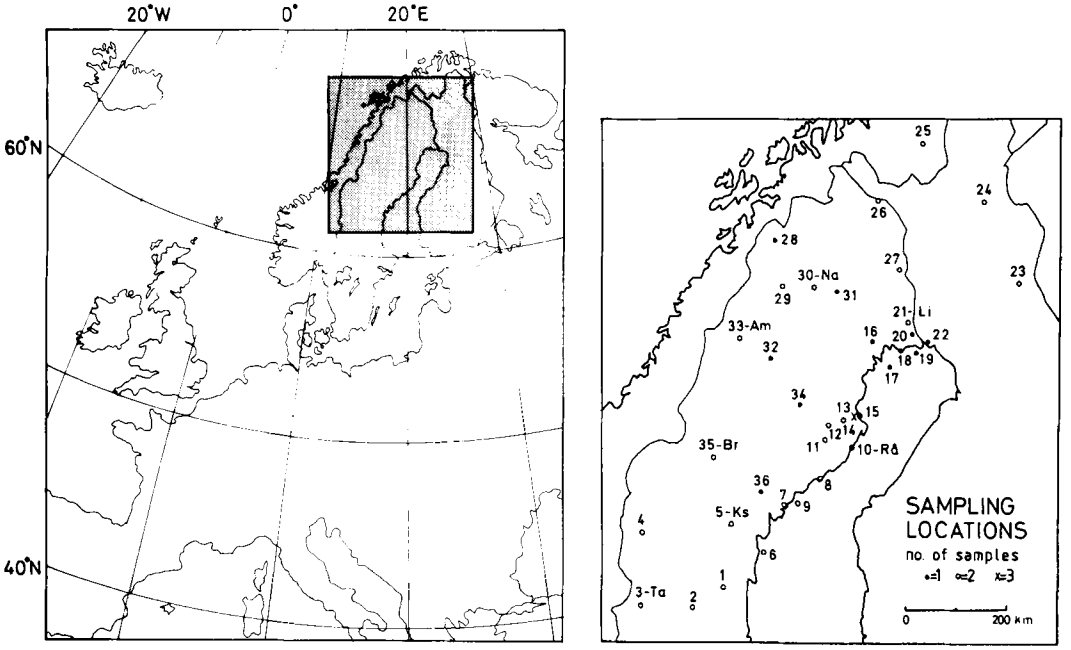

Fig. 1. Sampling locations of the snowpack. IMI rain chemistry stations are indicated by station codes.

at locations where the chemical composition of atmospheric precipitation is measured simultaneously and where dry deposition is unimportant (Cadle et al., 1984).

Northern Sweden is ideally suited for a snowpack survey in late winter because snow accumulates over several months, temperatures are nearly always below zero and solar insolation is low. Such surveys are important compliments to the ongoing trace metal monitoring programs, because little is known about the spatial variability of trace metal concentrations in atmospheric precipitation in the region.

It should be noted that special care must be taken when collecting and analyzing atmospheric precipitation samples for trace metals, because samples can be easily contaminated. Ross (1985) has shown that acidified samples can be contaminated if stored in bottles which have not been acid cleaned. The contamination of samples is due to desorption of metals from the container surfaces. Of the metals studied, risks for sample contamination was greatest for Cd, Cu and Zn. In some instances, Cu concentrations were 50 times higher in rain water samples collected and stored in equipment not previously washed in acid. Also, metals can adsorb onto the walls of the storage bottles. The adsorption is dependent on the metal, its concentration, the storage time and the container material. Problems with adsorption of metals can be avoided in conventional polyethylene bottles if the samples are acidified to a pH of 1.

2. Collection and analysis

2.1. Site location

In late February and early March 1984, snowpack samples were taken at 36 locations in northern Sweden, Norway and Finland (Fig. 1). 7 sampling sites were at International Meteorological Institute in Stockholm (IMI) Rain Chemistry Stations (Granat, 1980) and are designated in Fig. 1 by station codes. Sampling sites in the Baltic were on small islands. At 25 sites, duplicate samples were taken, and at 1 site triplicate samples.

Snow depth is highly dependent on the orographic features of the landscape. From previous studies, it has been found that small forest clearings are suitable locations for snowpack sampling. In this study, sampling sites were carefully chosen to be in such clearings and on level

ground free of bushes and snow drifts. Sites were approached by skiing at least 200–500 m away from roads and buildings to the sampling locations. The siting criteria were essentially the same as for the placement of IMI Rain Chemistry Stations (Granat, 1982).

2.2. Sampling methodology

Snowpack samples for major ion analysis, were taken with a three-walled polyethylene sampler. A large trench was first dug and the features of the snow deposition, as seen from the walls, were recorded. The sampler was inserted into the snowpack 10 cm from one of the walls so that the slot was facing towards the trench. To make certain the sample was taken on level ground free of bushes and other debris, the snow between the sampler and the wall was cleared using a plastic scraper. The first 2–5 cm of the snow inside the sampler was discarded to avoid contamination from the ground. The remaining snow inside the sampler was transferred to a water-washed plastic bag by inserting the scraper into the slot and working it downward. During sampling, shoulder-length polyethylene gloves were worn. Other clothing worn was made of terylene and had little tendency to give off dust. Snowpack samples taken with this device were representative of the total snow depth and hence the amount of water in the snow.

Samples for trace metal analysis were then taken. The sampling equipment was taken out from the transport bags and placed on the snow. Class 100 cleanroom protective clothing (with hood) and a new pair of plastic gloves were put on. A second wall of the trench was cut back about 10 cm using a specially designed scraping tool. The tool was constructed of high density polyethylene. It and the sample bottles had been previously washed for one month in acids according to the procedures of Ross (1984). The tool was stored in two plastic bags when not in use. A second pair of gloves were put on, and the sampling bottle (250 or 500 ml conventional polyethylene bottle) was then taken out of its two protective plastic bags and the lid removed. The total depth of the snowpack was sampled by running the bottle along the cleared wall using the lip of the bottle as a scraper. The bottle was closed and then placed in two new plastic bags.

Using the above procedures, duplicate samples were taken 50–300 m away.

2.3. Analytical methods

All samples were kept frozen until they were brought into the laboratory for analysis. Samples for major ion analysis were melted and transferred to conventional polyethylene bottles. Sulfate, nitrate, and chloride were determined using ion chromatography. pH was measured with a glass electrode and a separate reference electrode. Sodium, potassium, magnesium and calcium were determined with atomic absorption spectroscopy (flame) using the methods described by Ross (1983).

Samples for trace metal analysis were brought into a metal-free cleanroom and melted. They were then weighed and acidified to a pH of 1 with suprapur (Merck) nitric acid. Trace metal concentrations were determined using graphite furnace atomic absorption spectroscopy. A detailed description of sample handling to prevent contamination and analytical methods is given by Ross (1984).

Chemical blank studies were performed to determine whether samples were being contaminated by trace metals from the laboratory, in the field or during transport. Average metal concentrations in the laboratory and field blanks (5 of each) were approximately the same. Grand-average blank concentrations and standard deviations are given in Table 2.

3. Results and discussion

Trace metal concentrations and sulfate (as S) found in the snowpack and water equivalents are given in Table 1. Concentrations have not been adjusted for blank values.

3.1. Variability in the snowpack

In Table 2, the arithmetic mean, median and quartiles of the absolute difference between metal concentrations ($|C_1 - C_2|$) from samples taken at the same location are given. The median of the relative difference is smallest for Pb (10%) and highest for Fe (25%). The upper quartiles of $|C_1 - C_2|$ for Cu, Fe and Mn are less than the mean of $|C_1 - C_2|$. This indicates that there are outliers which greatly influence the mean values. The coefficients of variation, CV (ratio of the standard deviation to the mean) are a measure of the variability of $|C_1 - C_2|$, and are also given in Table 2. Zn had the lowest CV

Table 1. *Trace metal sulfate (as sulfur) concentrations in the northern Swedish snowpack, late winter 1984*

Site	H_2O (mm)	Cd	Cu ($\mu g\ l^{-1}$)	Fe	Mn	Pb	Zn	SO_4-S ($mg\ l^{-1}$)
1	195	0.060	0.43	16.9	1.67	3.37	3.85	0.58
	137	0.063	0.59	14.0	1.63	3.70	5.04	0.64
2	129	0.033	0.22	8.9	1.48	2.16	3.18	0.42
	144	0.033	0.38	11.4	1.51	2.05	3.13	0.38
3 (Ta)	201	0.041	0.23	14.0	1.03	3.28	3.61	0.44
	191	0.049	0.26	9.0	1.19	3.50	4.03	0.55
4	153	0.008	0.07	4.9	0.47	0.80	0.71	0.18
	183	0.015	0.11	5.2	0.58	0.87	0.90	
5 (Ks)	161	0.026	0.19	7.1	0.87	1.87	2.12	0.44
	131	0.032	0.25	10.1	1.03	2.03	2.48	
6	104	0.118	0.81	34.6	(6.16)	5.88	(9.67)	1.16
	144	0.090	0.70	28.8	4.21	4.66	7.42	0.95
7	273	0.126	0.92	20.9	2.99	6.33	(10.62)	
	231	0.107	0.84	31.4	3.16	5.46	8.32	
8	161	0.071	0.35	14.4	1.72	3.80	5.39	0.65
	206	0.079	0.60	16.1	2.05	4.16	6.07	0.66
9	206	0.061	0.56	18.7	1.58	4.13	5.13	0.62
	224	0.064	0.56	19.7	1.51	3.75	4.94	0.50
10 (Rå)	232	0.071	1.15	15.3	1.48	4.02	5.42	0.56
	235	0.074	1.10	15.2	1.50	4.28	5.92	0.55
11	189	0.076	0.59	15.2	1.63	4.08	4.55	0.51
	198	0.075	0.60	14.2	1.53	3.77	4.14	
12	134	0.032	0.64	9.8	1.06	2.14	3.49	
	171	0.037	0.47	9.4	0.85	2.37	3.38	0.41
13	173	0.046	0.63	10.2	0.93	3.01	4.07	0.35
	190	0.054	0.67	15.7	1.42	3.33	4.89	
14	161	0.104	1.84	20.0	1.70	6.80	8.04	0.50
	171	0.103	1.91	23.9	2.02	6.16	7.29	0.48
	134	0.126	(3.80)	29.2	1.94	6.99	8.12	0.46
15	184	0.277	20.0	25.2	2.20	25.0	24.0	0.58
	170	0.235	25.0	25.9	2.38	22.0	22.0	0.66
16	187	0.053	0.56	9.8	1.11	3.21	4.76	0.48
17	163	0.047	1.30	18.7	2.03	3.30	3.96	0.42
18	207	0.042	0.77	15.8	2.11	2.58	4.55	
19	171	0.049	0.69	(25.5)	(20.0)	2.72	(10.90)	
20	205	0.046	0.46	16.6	1.44	3.05	(10.20)	0.51
21 (Li)	222	0.046	0.50	12.3	1.35	3.08	4.75	0.42
	260	0.058	0.46	(32.0)	1.58	3.71	5.47	0.58
22	187	0.049	0.57	31.5	3.03	3.77	6.02	0.66
23	160	0.026	0.46	(77.1)	0.85	3.03	2.03	0.32
	132	0.021	0.57	14.2	0.81	2.07	2.27	0.23
24	239	0.021	0.57	9.2	0.69	1.39	1.69	
	298	0.035	0.46	11.9	0.96	1.90	2.26	0.34
25	168	0.011	0.17	3.7	0.22	0.68	0.51	0.18
	172	0.005	0.14	5.8	0.24	0.38	0.30	0.12
26	160	0.006	0.14	8.0	0.34	0.39	0.52	0.13
	182	0.008	0.19	10.4	0.42	0.57	0.63	0.15
27	185	0.019	0.34	11.4	0.69	1.33	1.63	0.24
	192	0.024	0.30	11.3	0.79	1.59	1.98	0.14
28	358	0.003	0.11	2.5	0.31	0.16	0.22	
29	231	0.017	0.10	3.6	0.44	0.99	1.16	
	248	0.011	0.16	4.6	0.36	0.80	0.68	
30 (Na)	158	0.009	0.11	18.5	0.52	0.68	0.92	0.13
	264	0.006	0.19	9.8	0.59	0.58	0.53	

Table 1.—*continued*

Site	H_2O (mm)	Cd	Cu ($\mu g\ l^{-1}$)	Fe	Mn	Pb	Zn	SO_4-S ($mg\ l^{-1}$)
31	170	0.23	0.30	12.3	0.91	1.75	2.31	0.26
32	178	0.013	0.23	11.2	0.68	1.20	1.13	0.22
33 (Am)	302	0.010	0.20	8.3	3.34	0.67	1.45	0.24
	318	0.012	0.23	9.6	(11.0)	0.85	2.12	0.21
34	174	0.021	0.25	9.8	0.67	1.58	2.11	0.23
35 (Br)	257	0.019	0.20	1.7	1.29	1.23	1.54	0.24
		0.018	0.19	6.9	0.66	1.27	1.30	0.26
36	169	0.38	0.34	20.5	1.48	2.21	2.41	0.42

Sampling sites are given in Fig 1. Station codes of International Meteorological Institute in Stocholm (IMI) Rain Chemistry Stations and concentrations considered to be outliers are in parentheses.

Table 2. *Measured and calculated parameters associated with errors and uncertainties in trace metal concentrations in the northern Swedish snowpack*

	b	s_b	s_v	S	$\lvert C_1 - C_2\rvert$				
					Mean	CV	median	quartiles	
	(units: $\mu g\ l^{-1}$ unless otherwise noted)							(lower)	(upper)
Cd	0.001	0.001	0.008	0.008	0.008 (22%)	125%	0.006 (18%)*	0.003	0.010
Cu	0.03	0.02	0.06	0.07	0.21 (25%)	524%	0.06 (21%)*	0.04	0.14
Fe	0.20	0.35	3.1	3.2	6.3 (33%)	192%	2.7 (24%)*	1.0	5.4
Mn	<0.05	<0.05	0.16	0.16	0.52 (20%)	288%	0.16 (14%)*	0.08	0.26
Pb	0.21	0.09	0.30	0.31	0.34 (15%)	170% 170%	0.26 (10%)*	0.18	0.44
Zn	0.05	0.125	0.35	0.37	0.57 (19%)	110%	0.42 (16%)*	0.20	0.74

* Median of the relative difference.

b = mean chemical blank concentration (grand average of 5 laboratory and 5 field blanks).

s_b = standard deviation of the chemical blank.

s_v = calculated variability in the snowpack (eq. (1)).

S = the total measured standard deviation associated with a metal concentration in the snowpack (eq. (2)).

In the calculations of S and s_v concentrations considered outliers (see Table 1 and Subsection 3.1) were not used.

$|C_1 - C_2|$ = absolute difference between samples taken at the same site.

CV = coefficient of variation in % (ratio of the standard deviation of $|C_1 - C_2|$ to the mean).

(110%) while Cu had the highest (523%). The other metals, Cd, Pb, Fe and Mn ranged between 125% and 288% in increasing order.

The criteria for deciding whether the highest metal concentration from duplicate samples was an outlier (i.e. the sample was contaminated) was set 2 times the upper quartile of $|C_1 - C_2|$ for the particular metal. (The criteria was not applied at site 15 because of the highly elevated concentrations at that site.) Of the single samples it was judged that number 19 was an outlier with respect to Fe, Mn and Zn, and number 20 for Zn. Values which were considered outliers are enclosed in parentheses in Table 1. In total, the number of outliers in the data set is less than 3%.

Differences in metal concentrations in samples taken at the same sampling site can be due to a variety of factors: the variability in the snowpack,

contamination during collection, errors arising from chemical analysis and/or sample handling in the laboratory. If one assumes that the various uncertainties are independent of each other, that they follow a Gaussian distribution, and that the errors do not depend on the absolute amount of metals in the sample, then the total standard deviation associated with a metal concentration (S) is:

$$S = (s_a^2 + s_b^2 + s_v^2)^{1/2}, \quad (1)$$

where s_b is the standard deviation of the chemical blank, s_a the standard deviation of the chemical analysis and s_v the true (unknown) variability of metal concentrations in the snowpack at any sampling location. S can be calculated from the set of duplicate samples using the following formula (Hallert, 1967):

$$S = \left[\frac{\sum_n (C_1 - C_2)^2}{2n}\right]^{1/2}, \quad (2)$$

where n is the number of sample pairs. Inherent in this formulation of S is that the true value of C is the mean of C_1 and C_2. Values of S are given in Table 2. s_a has been determined previously (Ross, 1984) and found to be less than 4% for identical samples. It is negligible compared to S. Also, values of s_b for all metals are much smaller than S (see, Table 2). Hence the principal component of S is s_v, the uncertainty in metal concentrations arising from variations in the snowpack.

It should be emphasized that S represents the uncertainty of individual metal concentrations, from any of the sample concentrations. From the above discussion this uncertainty is primarily due to the actual variation in the snowpack at the sampling location.

3.2. *Loss of ions from the snowpack*

In Table 3 are the major ion concentrations for the snowpack samples taken at IM Rain Chemistry Stations and the volume-weighted mean concentrations found in monthly precipitation samples (collected in plastic bulk collectors) for the months in which the snowpack accumulated. According to available meteorological data, the snowpack began to accumulate at stations Am, Br and Na in November, 1983. At the other stations it began to accumulate in December 1984. The precipitation data from stations Ta, Rå, Li and Am are the average from two samplers, the data from the other stations are from single samplers.

The concentrations of potassium, magnesium, and calcium approach the detection limit of the chemical analysis, and therefore are not suitable for comparison. With the exception of the data from

Table 3. *Major ion concentrations and water equivalent data for snowpack samples and volume-weighted monthly precipitation (bulk) samples from IMI rain chemistry stations for the months which the snowpack accumulated (S = snowpack, P = precipitation)*

Station	S/P	H_2O (mm)	Cl^- (mg l^{-1})	NO_3^- (as N) (mg l^{-1})	SO_4^{2-} (as S) (mg l^{-1})	Na^+ (mg l^{-1})	K^+ (mg l^{-1})	Mg^{2+} (mg l^{-1})	Ca^{2+} (mg l^{-1})	pH
Ta	S	185	0.52	0.27	0.46	0.30	0.03	0.04	0.05	4.40
Dec.–Feb.	P	155	0.50	0.29	0.57	0.26	0.02	0.04	0.04	4.40
Ks	S	162	0.16	0.31	0.44	0.12	0.02	0.02	0.04	4.39
Dec.–Feb.	P	130	0.20	0.31	0.45	0.09	0.02	0.02	0.04	4.42
Rå	S	247	0.36	0.36	0.55	0.23	0.03	0.03	0.05	4.38
Dec.–Feb.	P	158	0.57	0.40	0.70	0.29	0.07	0.06	0.05	4.36
Li	S	243	0.20	0.30	0.50	0.18	0.02	0.02	0.05	4.49
Dec.–Feb.	P	175	0.34	0.36	0.38	0.20	0.01	0.03	0.03	4.50
Na	S	159	0.07	0.15	0.13	0.09	0.02	0.02	0.03	4.83
Dec.–Feb.	P	89	0.23	0.25	0.38	0.09	<0.01	0.01	0.02	4.48
Am	S	312	1.31	0.11	0.22	0.68	0.06	0.09	0.07	4.84
Nov.–Feb.	P	169	0.61	0.13	0.19	0.29	0.03	0.04	0.04	4.79
Br	S	251	0.47	0.18	0.25	0.25	0.05	0.03	0.03	4.58
Nov.–Feb.	P	164	0.39	0.21	0.34	0.20	0.02	0.03	0.03	4.60

station Am, the maximum difference in sodium concentrations is about 30%. In contrast, chloride concentrations are more variable. At station Am there is 2 times more chloride in the snowpack than in the precipitation samples, while at station Na there is 4 times more chloride in the precipitation samples. At the other stations, the maximum difference is 40%. The difference in pH values is small, typically less than 0.02 pH units, with the exception of values from station Na. The larger differences in pH values at station Na can be explained by the higher concentrations of nitrate and sulfate in the monthly precipitation samples. In Fig. 2 the concentrations of nitrate and sulfate (in terms of N and S) in the snowpack are plotted against the volume-weighted mean precipitation concentrations. Nitrate in the snowpack is typically 5–10% less than what is found in monthly precipitation samples. Sulfate deviates to a greater extent, with a typical deviation of ±20%. The largest differences, for both nitrate and sulfate, are found at station Na. The deviation in the amount of precipitation between snowpack and monthly precipitation samples is substantial and variable, and is most likely due to the poor collection efficiency of the bulk samplers with respect to snow.

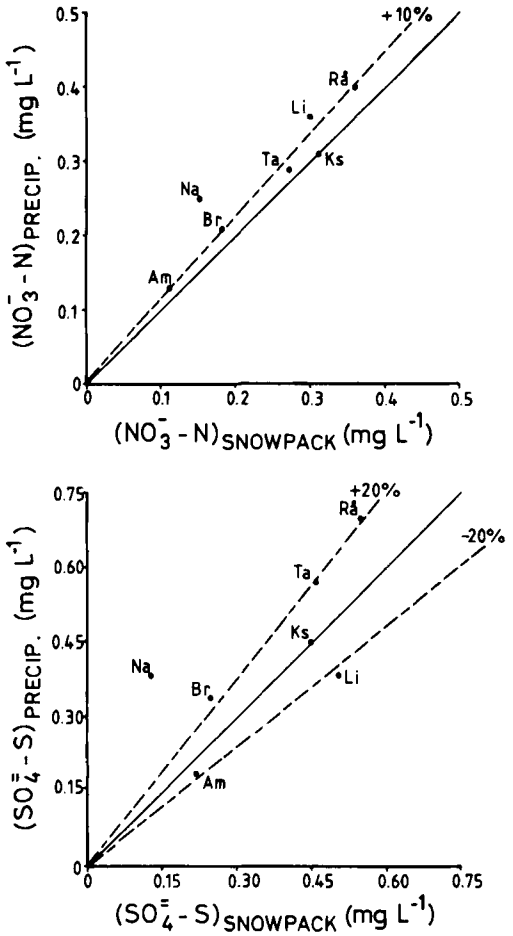

Fig. 2. Concentrations of nitrate and sulfate (as N and S, respectively) in the snowpack and monthly precipitation samples at IMI stations. Precipitation concentrations are volume weighted means. Sampling times are given in Table 3.

At stations Rå and Br and Ta, there is 20% less sulfate in the snowpack than what is found in the precipitation samples. The actual loss of sulfate from the snowpack at these stations may have been greater because the dry deposition velocities of particulate sulfate and gaseous SO_2 to plastic surfaces are smaller than to snow (Dasch, 1983; Ibrahim et al., 1983; Cadle et al., 1984). In Table 4 the 1983–1984 winter concentrations of atmospheric SO_2 and particulate sulfate at stations Rå and Br are given along with the calculated dry deposition of sulfur to snow. In the calculations the dry deposition velocity of SO_2 to snow was taken to be 0.1 cm s^{-1} (Granat and Johansson, 1983) and 0.07 cm s^{-1} for particulate sulfate (Ibrahim et al., 1983).

Assuming that there is no dry deposition of sulfur to plastic surfaces, the total deposition of sulfur (T) to snow during the winter would be:

$$T = D + (C_p)(mm_{sp}), \quad (3)$$

where D is the sulfur from dry deposition processes, C_p the concentration of sulfur in the precipitation samples and mm_{sp} the water equivalent of the snowpack. At station Rå the total deposition of sulfur would be 0.21 g m^{-2} and at station Br, 0.098 g m^{-2}. Dividing by the snowpack water equivalent data, the total concentration of sulfur in the snowpack would be 0.85 mg l^{-1} at station Rå and 0.39 mg l^{-1} at station Br.

The above calculations imply that about 15% of the sulfur in the snowpack at these stations is from dry deposition. A comparison of the calculated concentrations of sulfur in the snowpack and what was measured indicates that the maximum loss from the snowpack at stations Rå and Br is about 35%. These results should be tempered by the uncertainties in the calculations; the imprecise knowledge of dry deposition velocities and the

Table 4. *1983–1984 mean winter concentration of atmosphere SO_2 and particulate SO_4^{2-} at stations Br and Rå*

	Air concentrations ($\mu g\ m^{-3}$)		Sulfur dry deposition in the snowpack ($g\ m^{-2}$)
	SO_2 (as S)	Particulate SO_4^{2-} (as S)	
Rå (Dec.–Feb.)	3.7	1.5	0.15
Br (Nov.–Feb.)	0.82	0.56	0.05

The dry deposition of sulfur during winter months was calculated using a dry deposition velocity to snow of 0.1 cm s^{-1} for SO_2 and 0.07 cm s^{-1} for particulate SO_4^{2-}.

Table 5. *Least square coefficients of determination (r^2 in %) for trace metals and sulfate concentrations in the northern Swedish snowpack*

Cd	Pb	Zn	Fe	Mn	Cu	
89	**86**	**88**	56	53	33	SO_4^{2-}
	96	**90**	56	53	53	Cd
		94	59	51	57	Pb
			59	58	53	Zn
				55	38	Fe
					31	Mn

Regression calculations were performed excluding samples from sites 14 and 15. Number of points in the regression calculations are approximately 50 for metal pairs and 40 for metal–sulfate pairs. For all correlations, r^2 was non-zero (0.995 level of significance). Coefficients of determination greater than 0.85 are indicated in boldface.

variability in the amounts of precipitation. Also, the assumption that there was no dry deposition to the bulk collector and to the snow which accumulated in it during the sampling period may not be quite true.

It is concluded that, within 35%, the snowpack samples represent the volume weighted mean concentration of soluble ions in precipitation which fell during the winter months. The relatively small losses from the snowpack is more than likely due to that the sampling period was before the spring melt. Since little of the major ions have escaped from the snowpack, it is presumed that this would also be true for trace metals.

3.3. Spatial distribution of trace metal in the snowpack

In Fig. 3, trace metal concentration maps over northern Sweden are presented. Metal concentrations have been adjusted for blank values. When drawing isolines of concentration the variability of metal concentrations in the snowpack must be taken into account. Therefore, the minimum concentration isoline value was set equal to or greater than the upper quartile of $|C_1 - C_2|$.

For all metals, concentrations are highest along the Baltic coast and decrease towards the interior. Though, due to space limitations, further gradient lines along the coast were not drawn, the concentration gradients along the coast for all metals are stronger than in the interior. The highest metal concentrations for all metals except Mn and Fe are found at site 15. This site is 5 km west of a large smelter (Rönnskärverket). The smelter is the largest point source of atmospheric emissions of Cd, Cu, Pb and Zn in Sweden (SNV, 1982).

With the exception of Fe, the spatial distribution of metal concentrations are similar, and are also similar to concentration fields reported by Granat (1981) for sulfate, nitrate, ammonium and hydrogen ions. To quantify this similarity, a linear correlation analysis was performed. Samples from sites 14 and 15 were excluded because they were influenced by the large source in the near vicinity. In Table 5, the coefficients of determination (r^2) are given. The concentrations of sulfate, Cd, Pb and Zn

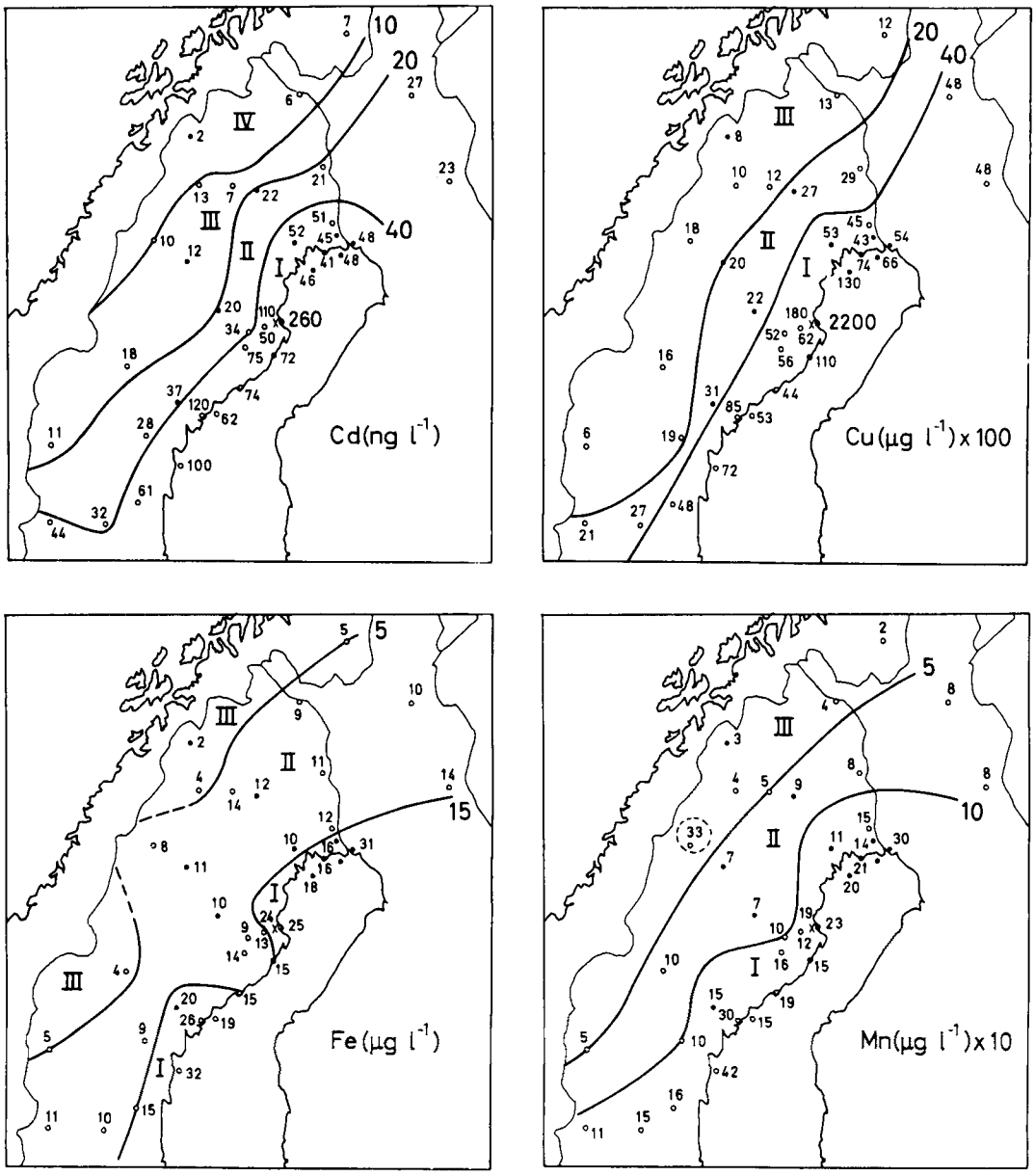

Fig. 3. Maps of trace metal concentrations in the northern Swedish snowpack, late winter 1984.

are very well correlated to one another (around 90%), while the concentrations of Cu, Fe and Mn have poorer correlations to sulfate, Cd, Pb and Zn and to one another (33–59%).

The coefficients of determination indicate that concentrations of Cu, Fe and Mn are not well correlated to concentrations of sulfate. However, an inspection of concentration plots (Fig. 4) indicate that a portion of these metals in the snowpack are correlated to sulfate. When compared to the plot of Cd to sulfate, the Cu, Fe and Mn data exhibits greater scatter. Also, higher concentrations of Mn and Cu deviate from trends established by lower concentrations. When the

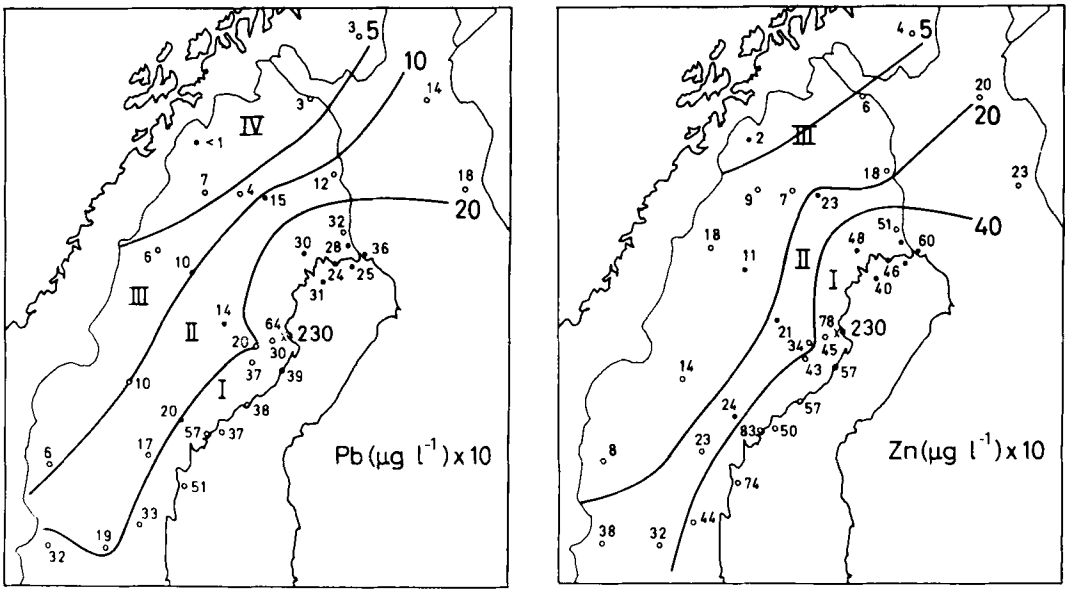

Fig. 3. (cont'd)

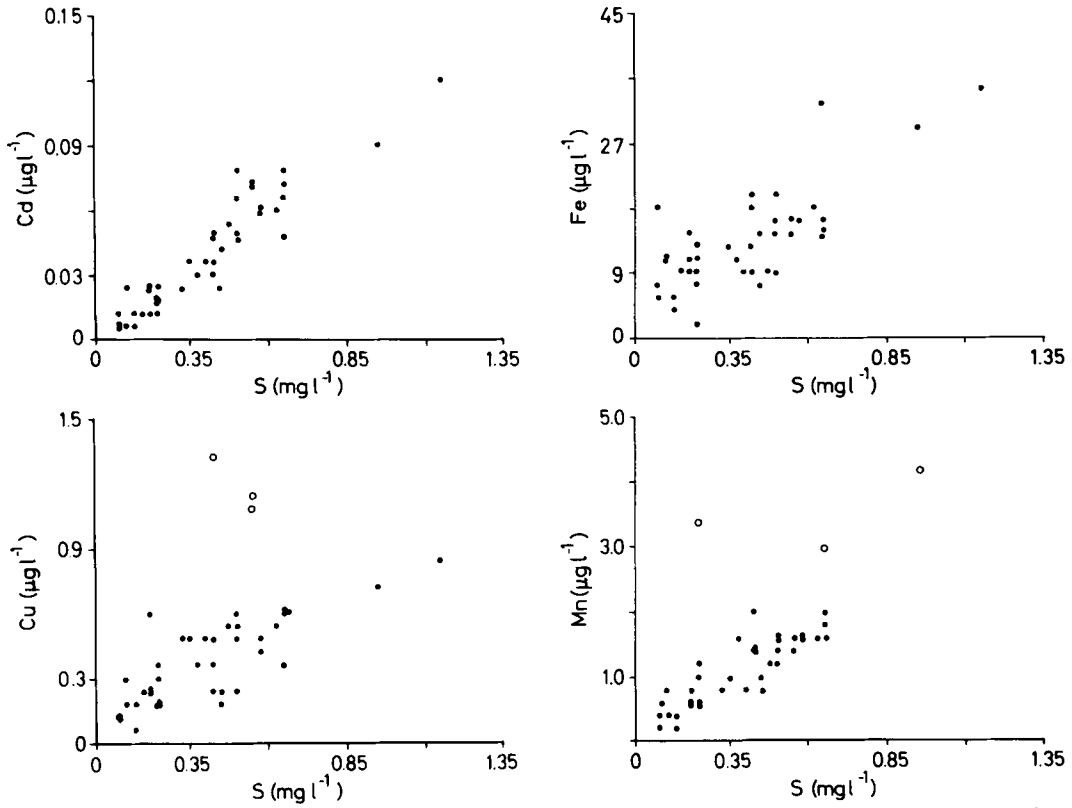

Fig. 4. Concentrations of Cd, Cu, Fe and Mn to sulfate in the northern Swedish snowpack. When the three highest concentrations of Cu and Mn are removed from the data set (points indicated by hollow circles) coefficients of determination (r^2) increase from 33 % to 63 % for Cu and from 53 % to 71 % for Mn.

three highest concentrations of Cu and Mn are removed from the data set, coefficients of determination increase from 33% to 63% for Cu and from 53% to 71% for Mn. The removal of the three highest Fe concentrations does not significantly alter the Fe to sulfate correlation.

To understand the deposition patterns of trace metals in northern Sweden one must take into account the geographic features of the region and the origin of precipitating air masses. Using 850 mb wind directions it was found that precipitation along the Baltic coast (northeastern Sweden) originates primarily from southerly air masses. In contrast, precipitation in mountainous regions (northwestern Sweden) was found to originate, in 60–90% of the cases studied, from air masses arriving from the north Atlantic (Persson and Kindell, personal communication).

As visualized in Fig. 5, the east to west gradients in metal concentrations in northern Sweden can be explained in the following way; precipitation in coastal regions of northern Sweden is mainly from polluted air masses advected from the south and southeast, while interior regions receive relatively unpolluted precipitation from northerly and/or northwesterly maritime weather systems. The east to west gradients are further enhanced by scavenging processes, along the western edge of the Scandinavian mountains, which cleanse relatively unpolluted air from the Norwegian Sea.

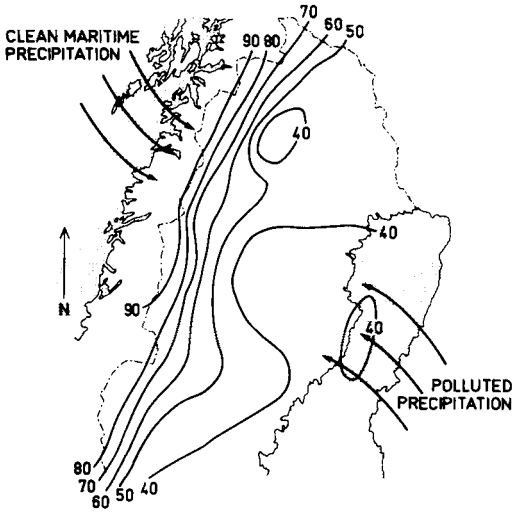

Fig. 5. Percent of total precipitation which falls from sector SW–NW over northern Sweden during the winter season (October–March). Values were calculated from observed 850 mb wind directions. (Courtesy of Christer Persson and Sven Kindell, Swedish Meteorological and Hydrological Institute.)

3.4. Metal concentrations compared to literature values

Mean snowpack metal concentrations for different regions, delineated by the concentration isolines in Fig. 3 are given in Table 6. These values are compared to volume weighted mean metal concentrations found in precipitation in southern Sweden (Ross, 1984) for the period November 1983 to February 1984. Mn and Fe concentrations along the coast (regions I) are about three times lower than concentrations found in precipitation in southern Sweden. Pb and Zn concentrations are about a factor of two lower. Concentrations of Cd and Cu are about 30% lower. Metal concentrations in the snowpack in the interior (regions III and IV) are typically a factor of ten lower than concentrations found in precipitation in southern Sweden.

The minimum trace metal concentrations in the snowpack from the eastern Canadian shield (Barrie and Vet, 1984) correspond to values found in regions II or III. With respect to other trace metal concentrations reported in the literature for rural regions, summarized by Galloway et al. (1979), metal concentrations in northern Sweden are substantially lower (see Table 6). Ross (1985) has suggested that a portion of these high metal concentrations may be attributed to sample contamination.

Lowest concentrations for all metals are found at sites in the Swedish mountains (sites 4, 28 and 29). For example, site 28 is in an elevated region (approximately 500 m above MSL) in a Swedish national park. For all metals this site had the lowest or second lowest concentrations. Minimum concentrations in the northern Swedish snowpack are comparable to concentrations found in accumulated snow in Greenland (Boutron, 1979) and in the European Arctic near Spitsbergen (Mart, 1983). Most recently, Batifol and Boutron (1984) have measured trace metals in high altitude snow at Mont Blanc, in the French Alps. Minimum concentrations in northern Sweden are about a factor of 2–25 lower (see Table 7).

At Jergul, Norway, precipitation was collected

Table 6. *Trace metal concentrations in the northern Swedish snowpack, precipitation from southern Sweden, snowpack from the eastern Canadian Shield and concentrations reported in the literature; concentrations from southern Sweden are the average of volume weighted mean concentrations from 2 sites (November, 1983 to February, 1984)*

	Northern Sweden				Southern Sweden[1]	Canada[2]	Literature[3]
	I	II	III	IV			
				($\mu g\ l^{-1}$)			
Cd	0.066	0.029	0.014	0.006	0.010		0.08–46
Cu	0.74	0.26	0.14		1.0	0.25–1.6	0.4–150
Fe	21	12	4		68		
Mn	1.8	0.8	0.4		6.4	0.55–5.2	0.2–84
Pb	3.7	1.7	0.7	0.4	7.3	0.8–12	0.59–64
Zn	5.5	2.8	1.0		11		<1–311

[1] Ross (1984).
[2] Barrie and Vet (1984).
[3] Galloway et al. (1982).

Table 7. *Minimum trace metal concentrations in the northern Swedish snowpack and trace metal concentrations in snowpacks from Greenland, European Arctic near Spitsbergen and Mont Blanc*

	Northern Sweden	Greenland[1] ($\mu g\ l^{-1}$)	European Arctic[2]	Mont Blanc[3]
Cd	0.002	0.0007–0.0085	0.003–0.006	0.054
Cu	0.08	0.036–0.102	0.080–0.120	0.18
Fe	2	1.53–28.3		6.3
Mn	0.3	0.030–0.438		1.3
Pb	<0.1	0.128–0.899	0.173–0.226	2.4
Zn	0.2	0.097–1.51		1.3

[1] Boutron (1979).
[2] Mart (1983).
[3] Batifol and Boutron (1984).

on a weekly and daily basis between August 1978 and June 1979 (Hanssen et al., 1980). The authors reported that yearly mean metal concentrations for Cd, Mn, Pb and Zn were 0.22, 4, 3.5 and 7.8 $\mu g\ l^{-1}$, respectively. Concentrations found in the snowpack in this study at the same location (sample concentrations from site 25 in Table 1) are about a factor of 10 lower.

3.5. *Deposition of trace metals in northern Sweden*

No clearly definable spatial gradients were seen for precipitation amount in northern Sweden for the sampling period. Therefore, to calculate metal accumulations per unit area, water equivalent data was averaged for each region for each metal. Trace metals accumulations per unit area and the total amount of metals in the snowpack for the part of Sweden shown in Fig. 3 are given in Table 8.

3.6. *Origin of trace metals in the snowpack*

Enrichment of trace metal concentrations in the snowpack with respect to soil dust can be assessed by calculating an enrichment factor (EF). An EF for element X is defined as:

$$EF = \frac{(X/Fe)_{snowpack}}{(X/Fe)_{crust}}, \quad (4)$$

where the mean composition of crustal material reported by Mason (1966) is used in the denominator. An EF approaching unity indicates

Table 8. *Accumulation of trace metals in the northern Swedish snowpack per unit area and the amount of metals contained in the snowpack*

Region	I	II	III	IV	Total
Cd:					
mm H_2O	190	160	200	280	
area (10^3 km^2)	63	77	92	45	
accumulation (μg m^{-2})	13	4.6	2.8	1.7	
amount deposited (tonnes)	0.79	0.36	0.26	0.08	1.49
Cu:					
mm H_2O	190	170	230		
area (10^3 km^2)	57	80	141		
accumulation (μg m^{-2})	141	44	32		
amount deposited (tonnes)	8.0	3.5	4.6		16.1
Fe:					
mm H_2O	180	190	250		
area (10^3 km^2)	32	188	57		
accumulation (μg m^{-2})	3.7	2.3	1.0		
amount deposited (tonnes)	119	429	57		606
Mn:					
mm H_2O	190	180	230		
area (10^3 km^2)	90	106	81		
accumulation (μg m^{-2})	340	140	92		
amount deposited (tonnes)	31	15	7		53
Pb:					
mm H_2O	190	160	220	260	
area (10^3 km^2)	76	92	71	40	
accumulation (μg m^{-2})	700	270	150	104	
amount deposited (tonnes)	53	25	11	4	93
Zn:					
mm H_2O	190	160	230		
area (10^3 km^2)	50	76	150		
accumulation (μg m^{-2})	1040	450	230		
amount deposited (tonnes)	52	34	35		121

that an element has little or no atmospheric sources other than wind blown crustal material. Crustal material is generally considered the major source of the metal when the EF is under 3. A large EF, greater than 10, indicates sources other than wind blown soil dust. In the absence of other natural sources in northern Sweden during winter months, this source would be anthropogenic emissions.

Mean EFs are given in Table 9. For regions I, II and III the order of decreased enrichment is Cd > Pb > Zn $\gg$ Cu > Mn. The relative enrichment for all metals (except Mn) decreases by about a factor of two as one goes inland. EFs for Cd, Cu, Pb and Zn indicate that they are primarily of anthropogenic origin. Also, Cu, Pb and Zn are enriched to a greater extent in precipitation in northern Sweden than in southern Sweden (see Table 9). EFs in northern Sweden are generally larger than those of the snowpack in the French Alps (Batifol and Boutron, 1984) and the Canadian snowpack reported by Barrie and Vet (1984).

Cd, Pb and Zn are highly enriched in the snowpack with respect to soil dust, and hence their major sources are anthropogenic. These metals are also highly correlated to sulfate in the snowpack. The deposition of sulfur in Sweden has been shown to be mainly governed by long-range transport of anthropogenic emissions from other European countries (OECD, 1977; Eliassen and Saltbones, 1983). Therefore, it is concluded that the deposition of Cd, Pb and Zn in northern Sweden in winter months is also primarily due to long-range trans-

Table 9. *Calculated enrichment factors (EF) with respect to crustal material (Fe as the reference element) in the northern Swedish snowpack, precipitation from southern Sweden, and the snowpack from Mt. Blanc; EF values from southern Sweden are 1984 volume weighted mean values*

	Northern Sweden						Canada[2]	
	I	II	III	IV	Southern Sweden	Mt. Blanc[1]	range	mean
Cd	1003	664	508	247	5600	900		
Cu	42	20	18		18	4.5	3.4–47	29
Mn	6	4	4		5.9	1.4	1.0–11	3.4
Pb	881	609	364	406	537	270	34–400	100
Zn	240	180	100		162	28		

[1] Batifol and Boutron (1984).
[2] Barrie and Vet (1984); Al is used as the reference element.

port of anthropogenic emissions from the European continent.

The relatively high EF of Cu in the snowpack indicates that it is of primarily anthropogenic origin. The regional distribution of Cu and sulfate in the snowpack are similar (see Fig. 3), though the correlation of Cu and sulfate in the snowpack is poorer than the correlations of sulfate, with Cd, Pb and Zn. Since anthropogenic emissions of Cu are associated with larger particles, than emissions of Cd, Pb and Zn (Bacci et al., 1983; Chan et al., 1983; Rahn, 1976) the scatter in the Cu to sulfate plot may be due to local anthropogenic sources. On the whole, however, it would appear that a large portion of the Cu is also supplied by long-range transport.

The EF of Mn indicates it has an appreciable soil source. Since most of northern Scandinavia is covered by snow and ice, a large local soil source seems unreasonable. As seen from the Mn to sulfate plot (Fig. 4), the lower concentrations of Mn, are well correlated to sulfur concentrations. Therefore, it is also thought that a significant portion of the Mn in the snowpack is supplied by long-range transport.

In Fig. 6 metal concentrations in the snowpack are plotted against distance from Rönnskärverket. Concentrations have been divided by the mean concentration of the region where the site is located. At 5 km from the smelter, concentrations of Cd, Cu, Pb and Zn are much higher in the snowpack relative to mean concentrations in region I. With increasing distance from the smelter Cu concentrations decrease more rapidly than concentrations of Cd, Pb and Zn. At a distance of 20 km from the smelter Cu concentrations are 5% of the value at 5 km, while Cd, Pb and Zn concentrations are about 15–25%. Between 20 and 40 km from the smelter, Cd, Cu, Pb and Zn concentrations are at region I levels. The relatively small elevation of Fe and Mn concentrations in the snowpack at 5 km from the smelter, and the relatively large deviation of their concentrations from mean regional values indicates that the Fe and Mn concentrations in the snowpack are not greatly elevated due to the smelter.

It can not be determined to what extent emissions from the smelter influence regional scale trace metal concentrations. However, the spatial pattern of trace metal concentrations in the snowpack (see Fig. 3) indicate that it is unlikely that emissions significantly influence metal concentrations beyond 40 km from the smelter. We therefore view these results as further evidence that much of the metal deposition in northern Sweden is from long-range transport.

4. Conclusions

It is concluded that large scale regional snowpack surveys are useful tools for studying the spatial variability of trace metal deposition during winter months. If the sampling period is before the spring thaw, and the snowpack is not subjected to winter meltings, ion concentrations in the snowpack seem to be stable.

Trace metal concentrations in precipitation in northern Sweden are lower than concentrations found in southern Sweden. Metal concentrations in

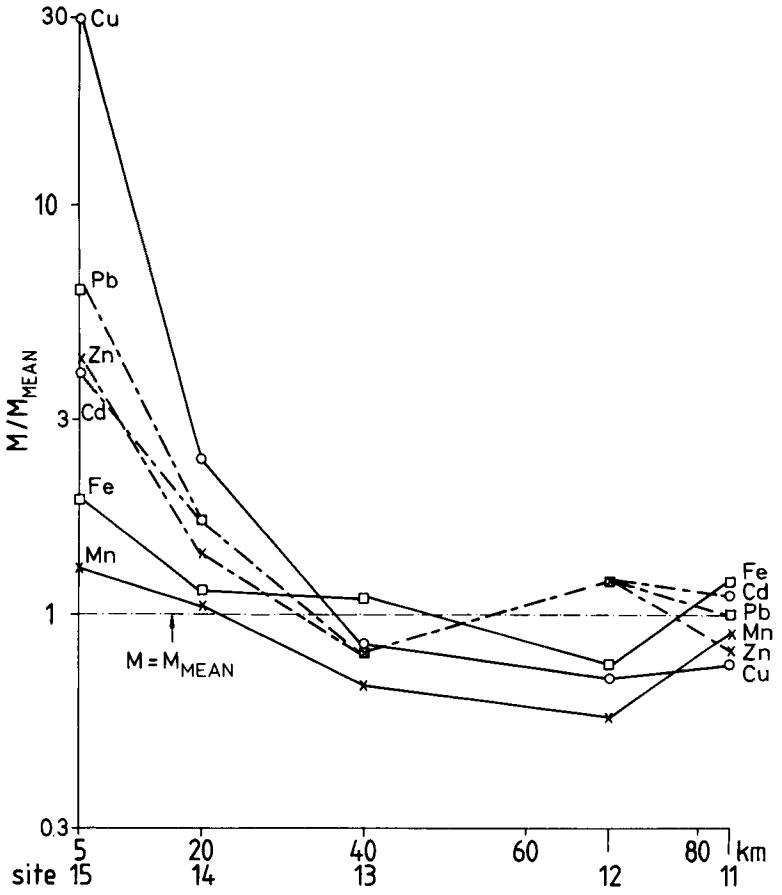

Fig. 6. Concentration of trace metals in the snowpack with respect to distance from Rönnskärsverket, a large smelter. Metal concentrations have been divided by the mean concentration of the region where the site is located. At a distance of 20–40 km from the smelter, concentrations of Cd, Cu, Pb and Zn are at mean levels found in region I (indicated by the broken line).

northern Sweden decrease from the Baltic towards the interior. In remote regions in northwestern Sweden metal concentrations are very low and approach levels found in Greenland and the European Arctic near Spitsbergen. It is thought that the concentration fields in the area are due to that deposition along the Baltic coast is mainly from polluted air masses advected from the south and east, while interior regions receive more precipitation from northerly and/or northwesterly maritime weather systems.

It is concluded that the major source of Cd, Pb and Zn in the northern Swedish snowpack is the long-distance transport of anthropogenic emissions from Europe. In addition, the high correlation of Cd, Pb and Zn with sulfur in the snowpack indicates that the processes governing the deposition of sulfur and these metals on the average are similar. This correlation warrants further investigation since these elements have different atmospheric sources and undergo different atmospheric transformations than sulfur. Major sources of Pb in Europe are automobile exhausts (60%) and metal production (32%), while Zn and Cd sources are predominantly metal refining and smelting (Pacyna, 1984). In Europe, sulfur is predominantly released to the atmosphere from fossil fuels as gaseous SO_2. It would also be interesting to determine if the correlation of these elements will be the same during summer, when

other pathways are available for the conversion of SO_2 to sulfate.

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