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Observations on acidity and ions in East Greenland precipitation

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ABSTRACT

Precipitation collected in East Greenland by a wet-only type of collector for two years, has been analysed for all major ions. The concentrations are lower by a factor of 10 compared to a rural site in Denmark and somewhat lower than at the Faroe Islands. A pH value of 5.16 seems to be representative of arctic precipitation. Three discernible components appear to be present, a sea-spray and a crustal component and a component related to long-range transported aerosols from distant combustion sources. The total wet deposition is very small, but the risk of an effect on the sensitive arctic environment cannot be discarded without further assessment.

1. Introduction

The understanding of the acid precipitation phenomena and of the impact of human activities on the global environment requires information on the precipitation chemistry in remote areas. Such endeavour has been undertaken in the Global Precipitation Chemistry Project, GPCP, (Galloway and Gaudry, 1984) as well as in snow pack studies in remote arctic and antarctic regions (Barrie and Vet, 1984, Davidson et al. 1981, 1985, Neftel et al. 1985, Herron 1982). Snow pack studies and ice-core studies have been reported from the Greenland ice-sheet (Hammer et al., 1980, Busenberg and Langway, 1979). However, reports on chemical characterization of directly collected arctic precipitation are scarce (Dayan et al., 1985) and we are not aware of any published reports on wet-deposition in Greenland.

The present work is part of the SAGA-project (Studies on Aerosols in the Greenland Atmosphere) which has been conducted from 1979 to 1983 (Heidam, 1983, 1984). The main object of this work was to establish the sources contributing to the atmospheric aerosol.

Following Junge (1977) it can be argued that, under clean air conditions, the concentrations of trace substances in precipitation are, in general, proportional to the atmospheric concentrations. In a source-free area such as the Arctic a constant mixing ratio of aerosols in the lower troposphere can be assumed. The aged aerosol particles act as ice nuclei or as condensation nuclei for cloud droplets, and are deposited during precipitation. This removal mechanism dominates for particle sizes up to 5 μm. For larger particles, impaction scavenging by falling raindrops or snow flakes dominates. In both cases the resulting concentration in precipitation is approximately proportional to the concentration in the precipitating air mass.

2. Experimental

Precipitation was collected with a wet-only type of collector on a roughly monthly basis from April 1981 to April 1983. No distinction between rain and snow was made. Collection took place at the SAGA site at Mestersvig airfield in Eastern

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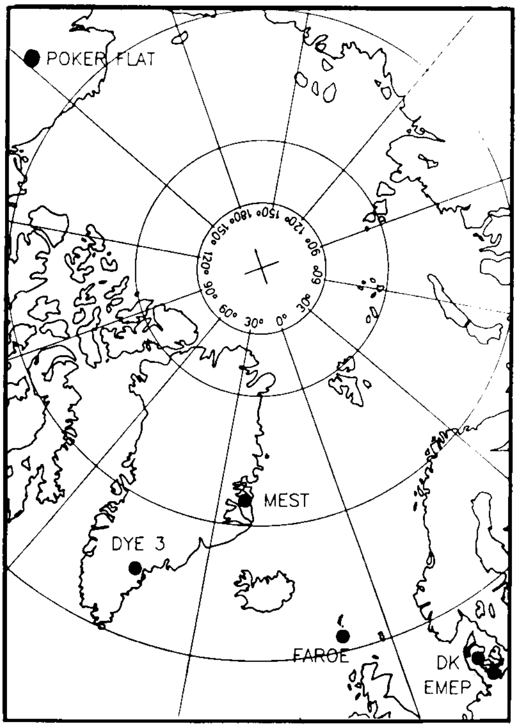

Fig. 1. Locations of sites mentioned in text: MEST—the observation at Mestersvig airfield; DK-EMEP—the two EMEP stations in Denmark proper; FAROE—the EMEP station at the Faroe Islands; DYE 3—observation site on Greenland icecap (Busenberg et al., 1979; Davidson et al., 1985); POKER FLAT—observation site in Alaska (Dayan et al., 1985).

Greenland (see Fig. 1) and was supervised by local technical personnel.

The airfield is situated on a plain on the southern coast of Kong Oscars Fjord, north of the Stauning Alps that reach 2500 m and more. The permanent staff is about 30. Local pollution sources are gas-oil burners in various buildings SSW of the main tower, exhausts from a few motor vehicles and an occasional aircraft, which may also raise dust in the summer. The air traffic is slight. Occasionally refuse burning takes place a few kilometers to the southeast. The sampling site was chosen on top of the tower to get away from these sources. Unfortunately there are also oil burner and ventilation exhausts on the tower roof. The sampling point was on the northernmost corner of the roof, upwind of these exhausts with respect to the most frequent WNW winds. More details on the site are given by Heidam (1983).

Under these experimental conditions there is a risk that local contamination may be important. Results from the SAGA-project on concentrations of elements in the atmospheric aerosol show, however, that concentrations at Mestersvig are similar to those found at other SAGA-sites, where local contamination is negligible. For soil-derived elements, annual concentrations at Mestersvig are about twice as large as in northern Greenland. In summer the concentrations are larger by a factor 2–10, stressing the need for a wet-only type of collector. In winter, however, the soil-derived elements are less abundant at Mestersvig by a factor 1–3 as compared to northern Greenland.

For pollution-derived elements, e.g. sulphur, zinc and lead, annual concentrations at Mestersvig are typical of those found elsewhere in Greenland, particularly during summer; in winter the concentrations at Mestersvig are relatively lower by a factor 1–5. As regards local contamination of precipitation, the suspect ions $SO_4^=$ and NO_4^- are both secondary pollutants that arise through oxidation of SO_2 and NO/NO_2, respectively. These oxidation processes require a certain length of time to become significant. At the prevailing low temperatures, this oxidation time is certainly longer than any primary pollutant of local origin resides in the area. The local contamination, if any, is therefore considered to be insignificant.

To ensure against changes in composition of the samples by microbiological activity, the samples collected were held refrigerated in darkness until shipping to the laboratory in Denmark, where they were also kept refrigerated until analyis was performed (Ridder et al., 1985). During collection, the sample was subjected to similar conditions, the sampling bottle was placed in darkness in the inside of the collector and ambient temperatures were generally low. The anions and the mono-valent cations were determined by thermostated (32°C) ion-chromatography. Analysis was performed for five samples followed by analysis of five standards. The reported values are means of three independent runs, and the average error is 10–15% with the exception of K^+ for which the uncertainty is larger owing to interference from NH_4^+. pH was measured with a combined electrode with 100 μl-saturated KCl-solution added per 5 ml of precipitation sample. Ca^{++} and Mg^{++} were determined by AAS. The precipitation volume was determined gravimetrically.

3. Results

In Table 1 the sampling characteristics of the 13 samples obtained are listed. Samples 3 and 6 were unintentionally exposed for several months. In view of the sampling conditions described above, it is nevertheless believed that valid results on ionic composition have been obtained for these samples also. Samples 1, 2 and 8 were excluded, however. In sample 1 the Na- and Cl-concentrations were atypically high, indicating a dominating marine deposition, and in sample 8 the Ca^{++}- and NO_3^--concentrations were atypically high, indicating a dominating soil-dust deposition. For this latter sample the number of openings is very low compared to the number of hours open, and it is believed that the sampler was not working properly but remained open in dry periods also. For sample 2 the volume collected was just too small to permit a meaningful analysis.

It is known that even wet-only samplers cannot fully discriminate between wet and dry deposition. Light fog is able to activate the sensor-plate, so the sampler may be open in situations with practically no wet deposition, and the number of openings cannot be regarded as a measure of independent precipitation events. In addition, gaseous transport and dry particulate deposition under the rim of the lid may occur when high winds cause slight openings of the lid. These effects are considered minor, and the remaining ten samples are believed to represent wet deposition. Thus a total amount of 4370 ml precipitation, corresponding to 140 mm of rain, collected over 480 days of exposure, was analysed.

In Table 2 the analytical results are listed in units of $\mu mol \cdot l^{-1}$ (μM). Also listed are the total anionic and cationic contents and their differences as well as the arithmetic means and standard errors. Results below detection limits are not shown, but they are included in the means and standard errors as zero.

4. Discussion

From Table 2 it is recognized that the total cationic concentrations resemble the total anionic concentrations and that deviations from a 1:1 relationship occur as excess cation-concentrations in samples with a high pH. From considerations

Table 1. *Sampling characteristics*

Sample number	Start	Expos. days	Volume ml	Hours open	Times open
1[a]	1981 Apr 01	30	12	15	39
2[a]	1981 May 01	32	3	53	157
3[b]	1981 Jun 02	152	1300	208	667
4	1981 Nov 12	19	100	137	8
5	1981 Dec 31	32	10	3	3
6[b]	1982 Feb 01	120	1400	248	449
7	1982 Jun 01	30	10	33	173
8[a]	1982 Jul 01	31	600	593	40
9	1982 Aug 01	31	50	327	135
10	1982 Sep 01	30	450	54	120
11	1982 Oct 01	18	840		
12	1983 Jan 12	20	80		
13	1983 Feb 01	28	130	66	148

[a] excluded from further analysis (see text)

[a] unattended for a long period (local strike)

Table 2. *Precipitation at Mestersvig. Ion concentrations in μM*

	H^{+a}	Na^+	K^+	NH_4^+	Ca^{++}	Mg^{++}	Cl^-	NO_3^-	$SO_4^=$	Q^{+b}	Q^{-b}	Qdiff[b]
Start												
1981 Jun 2	5.00	19.6		0.70	6.20	5.80	21.8	11.5	8.10	49.3	49.5	−0.2
1981 Nov 12	5.00	3.50	3.90	7.20			3.90	8.50	5.70	19.6	23.8	−4.2
1981 Dec 31	2.00	20.9	1.50		10.2	10.3	16.6		5.60	65.4	27.8	37.6
1982 Feb 1	11.0	0.90		9.30			2.90	6.50	5.70	21.2	20.8	0.4
1982 Jun 1	40.0	8.10		38.3	11.2	5.80	12.7	32.7	38.6	120.4	122.6	−2.2
1982 Aug 1	17.0	2.80		9.30	3.70	2.90	4.70	9.00	12.3	42.3	38.3	4.0
1982 Sep 1	1.00	2.20		6.20	9.20	4.50	4.50	5.80	3.30	36.8	16.9	19.9
1982 Oct 1	4.00	7.40	3.30	3.60			8.90	2.10	3.60	18.3	18.2	0.1
1983 Jan 12	13.0	21.3		1.90	3.20	6.60	25.1	9.70	11.3	55.8	57.4	−1.6
1983 Feb 1	12.0	14.8	1.80	6.40		4.10	12.3	8.60	11.2	43.2	43.3	−0.1
mean	11.00	10.15	1.05	8.29	4.37	4.00	11.34	9.44	10.54	47.23	41.86	5.37
S.E.	3.63	2.60	0.48	3.50	1.44	1.07	2.48	2.81	3.28	9.54	9.99	4.17

[a] H^+ calculated as 10^{6-pH}
[b] units: μEq

of the H_2O–CO_2 equilibriums it is reasonable to assume that measurement of HCO_3^- could have led to ion-balance. If the CO_2–H_2O equilibrium system is considered with a constant CO_2-pressure, one obtains

$$[H^+][HCO_3^-] = k_1 \cdot [H_2CO_3] = k_1 k_2 \, P_{co_2} = k$$

$$[HCO_3^-] = k \cdot \frac{1}{[H^+]}$$

The relationship between the ion-difference and the inverted hydrogen concentration is shown in Fig. 2. Orthogonal regression analysis yields a k·value of 34 μM^2. Allowing for P_{co_2} to vary in the range 400–700 ppm, which is representative of laboratory air during analysis, k·values in the range 25–40 μM^2 are found, and so some of the ion-difference seems explainable by the CO_2–H_2O equilibrium system. Considering the high variability of CO_2-pressure during analysis and the possible complex-formation involving HCO_3^-, the data presented neither confirm nor contradict the hypothesis suggested. The absence in ion-chromatographic analysis of F^--traces, the second most likely candidate, does, however, lend some support to the carbonate hypothesis.

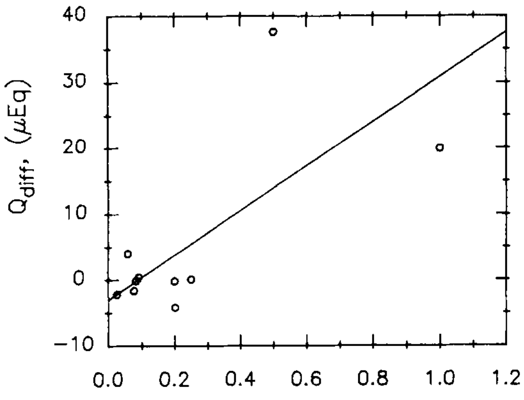

Fig. 2. Ion-balance off-set versus the inverted hydrogen-ion concentration.

Volume-weighted mean values are listed in Table 3 along with other data. Within the framework of the European Monitoring and Evaluation Programme (EMEP), a cooperative programme to evaluate long range transport of air pollutants over Europe (Eliassen and Saltbones, 1983), three stations are operated by Denmark, one in the Faroe Islands and two in Denmark proper. Precipitation-weighted annual mean concentrations are presented in Table 3 for 1982 (Heidam, 1986); for Denmark proper the values have been pooled. Concentrations in surface snow collected by other workers at DYE 3 in central southern Greenland as well as precipitation data from Poker Flat, Alaska are also included (Fig. 1). It is seen that the concentrations in Greenland agree with those from Alaska with the exception of Na, Cl, Mg, and

Table 3. *Geographical distribution of concentrations, μM*

Location period	DYE 3[a] 1974–75	DYE 3[b] 1978–83	MEST[c,d] 1981–83	Faroe[d,e] 1982	Denmark[d,e] 1982	Alaska[d,h] 1979–82
pH			5.16	5.18	4.33	5.11
H^+			6.87	6.68	46.4	7.8
Na^+	0.31	0.08–0.8	9.04		170[f]	0.5
K^+		–0.2	0.79			0.6
NH_4^+	0.32		5.09	16.1	49.7	3.5
Ca^{++}	0.18	0.01–0.35	3.02		14.9[f]	2.05
Mg^{++}		0.02–0.4	2.55		24.1[f]	0.65
Cl^-	0.59		10.9	3200	128	2.7
NO_3^-		0.8–5.5	7.32	13.7	44.4	1.9
$SO_4^=$	1.24	0.5–3.2	6.22	35[g]	46.3	6.15[g]

[a] Busenberg and Langway, 1979; snow samples
[b] Davidson et al., 1981, 1985; ranges for snow samples
[c] this work
[d] volume weighted means; pH = 6 − log H^+
[e] Heidam, 1985
[f] June 1983–May 1984
[g] non-marine value
[h] Dayan et al., 1985; polar flow into Poker Flat

NO_3, that are larger in Greenland. It is hardly surprising that the marine influence on the east coast of Greenland is larger than in the Alaskan interior, but it is noteworthy that nitrate is more conspicuous in Greenland. As argued later, it is presumably of distant anthropogenic origin.

The decrease in concentrations in precipitation from a rural site in Denmark to a site on the Faroe Islands to the east coast in Greenland is evident. The most likely causes for this decrease are scavenging processes. The levels in Greenland are less than at the Faroe Islands, but not very much less. In fact the pH-values around 5.16 hardly change at all. As a value of pH = 5.12 in precipitation collected from a ship in the Arctic ocean during summer has also been reported (Winkler, 1983), there seems to be some evidence that arctic precipitation in general has a pH at this level.

However, the concentrations in surface snow at an elevation of 2500 m are still lower. Hammer et al. (1980) report a background value of $H^+ = 1.2$ μEq (pH = 5.92) in ice cores. It is rather doubtful, however, if concentrations on the coast and at sea level can be compared with concentrations in snow in the interior of the ice cap at elevations of a thousand metres or more. Often the air masses residing over these two regions have quite different origins, and local meteorological conditions governing precipitation are also quite different.

The total wet deposition at Mestersvig through the two year period is shown in Table 4 together with the annual wet depositions at the Faroe Islands and in Denmark. Unfortunately the Greenland samples are too scattered over the period to allow annual rates to be determined (cf. Table 1). Annual precipitation rates are about 250 mm at Mestersvig, 500 mm in Denmark and 900 mm in the Faroes. It is seen that in comparison the deposition in East Greenland is very small. The environmental effects cannot be judged, however, without knowledge of the soil chemistry in these areas, in particular the buffering capacity.

From Table 2 it is evident that Na^+ correlates well with Cl^- on a mole-to-mole basis. With the analytical precision obtained, it is justifiable to assume that these species arise from the same source, namely seaspray. Thus either species can be used for sea-salt correction. By using published values for concentrations in seawater (Brewer, 1975), corrected values for K^+, Mg^{++}, Ca^{++} and $SO_4^=$ are calculated as means of the respective Na^+ and Cl^- corrections and listed in Table 5. A comparison with Table 2 shows that

Table 4. *Wet deposition*

MEST: μmol/m^2
Faroe and Denmark: mmol/m^2

	H^+	Na^+	K^+	NH_4^+	Ca^{++}	Mg^{++}	Cl^-	NO_3^-	$SO_4^=$
MEST									
1981–83	890	1140	100	640	380	320	1375	925	785
Faroe									
1982	7.09	—	—	13.6	—	—	$4.75 \cdot 10^3$	9.8	29.4[a]
Denmark									
1982	21.3	67.1[b]	4.27[b]	25.6	5.89[b]	9.51[b]	61.6	21.6	22.3

[a] non-marine value
[b] June 1983-May 1984

Table 5. *Total and non-marine concentrations in μM.*

Ion	H^+	Na^+	NH_4^+	Cl^-	$^*K^+$	$^*Ca^{++}$	$^*Mg^{++}$	$^*SO_4^=$
Start								
1981 Jun 2[a]	5.0	19.6	0.70	21.8	0.0	5.78	3.62	6.95
1981 Nov 12	5.0	3.50	7.20	3.90	3.83	0.0	0.0	5.49
1981 Dec 31	2.0	20.9	0.00	16.6	1.12	9.82	8.30	4.54
1982 Feb 1[a]	11.0	0.90	9.30	2.90	0.0	0.0	0.0	5.60
1982 Jun 1	40.0	8.10	38.3	12.7	0.0	11.0	4.72	38.0
1982 Aug 1	17.0	2.80	9.30	4.70	0.0	3.63	2.51	12.1
1982 Sep 1	1.0	2.20	6.20	4.50	0.0	9.13	4.16	3.12
1982 Oct 1	4.0	7.40	3.60	8.90	3.14	0.0	0.0	3.15
1983 Jan 12	13.0	21.3	1.90	25.1	0.0	2.73	4.17	10.0
1983 Feb 1	12.0	14.8	6.40	12.3	1.52	0.0	2.66	10.4
mean	11.00	10.15	8.29	11.34	0.96	4.21	3.01	9.94
S.E.	3.63	2.60	3.50	2.48	0.46	1.40	0.83	3.27

[a] long exposure

these non-marine components in general constitute more than 80% of the total concentrations. They are presumably of continental origin, except that $SO_4^=$ is considered to be anthropogenic.

In Table 6 the correlation coefficients for the components in Table 5 are shown. The correlations should be viewed with some caution since they refer to concentrations determined in only ten samples with a very wide range in precipitation volume and collection periods. All coefficients numerically lower than 0.4 have been deleted as nonsignificant at a 5% level of significance. With this simplification, the correlation matrix resembles a matrix in which most off-diagonal elements are zero. The non-zero values are large and tend to group into small square matrices along the main diagonal. Within each group the ions are thus strongly correlated but group-to-group correlations are small. Thus the ions tend to separate into three mutually independent groups.

The Na Cl group is evidently a marine component in the precipitation.

The second group consists of H^+, NH_4^+, NO_3^- and $^*SO_4^=$. Studies of the atmospheric aerosol in Greenland has led to the concept of an aerosol component with sulphate as the most prominent constituent, originating from a variety of combustion processes in populated, midlatitude regions (Heidam 1984). The strong correlation between the non-marine, i.e. anthropogenic, sulphate and the other components in the group indicate that they are all predominantly of distant

Table 6. *Significant non-zero correlation coefficients* ($|r| > 0.4$)

	Na^+	Cl^-	H^+	NH_4^+	NO_3^-	$*SO_4^=$	$*Ca^{++}$	$*Mg^{++}$	$*K^+$
Na^+	1	0.94	—	—	—	—	—	0.63	—
Cl^-		1	—	—	—	—	—	0.56	—
H^+			1	0.91	0.91	0.97	—	—	—
NH_4^+				1	0.90	0.93	—	—	—
NO_3^-					1	0.95	0.40	—	—
$*SO_4^=$						1	0.45	—	—
$*Ca^{++}$							1	0.82	−0.51
$*Mg^{++}$								1	−0.46
$*K^+$									1

anthropogenic origin. Presumably this ion group is the precipitation counterpart of the long-range transported aerosol component of anthropogenic origin.

The third group consists of non-marine Ca and Mg and is presumably a crustal component of distant or indigenous origin or both (Heidam, 1984). A component with this composition could explain the suggested occurrence of bicarbonate in the alkaline samples. This group also includes non-marine K, but with opposite polarity. This may well be an artifact of the analysis, because K is poorly determined.

5. Conclusion

The present study of precipitation in East Greenland, collected by a wet-only collector over 2 years, seems to indicate that the precipitation is polluted, albeit at low levels, but otherwise in much the same way as in more populated areas of the world.

It appears that ion-balance is attained within the analytical error, however, under the assumption that the cationic excess at high pH is caused by the absence of HCO_3^--measurements. Subject to this qualification, all major ions appear to have been taken into account.

The concentrations which agree with observations from Alaska are about an order of magnitude lower than at a rural site in Denmark and somewhat lower than at a background site on the Faroe Islands. However, a value of pH $\sim$ 5.15 seems to be representative of both the arctic and sub-arctic precipitation at sea level. For the ions K^+, Mg^{++}, Ca^{++} and $SO_4^=$, more than 80% of the concentrations were non-marine and presumably of continental and distant anthropogenic origin.

The depositions in East Greenland over the 2-year observational period were lower by at least one order of magnitude than annual deposition rates at the Faroe Islands and in Denmark. However, to elucidate the environmental consequences, additional investigations are needed.

The arctic precipitation at sea level seems to contain at least three components. The sea spray and the crustal components are of natural origin, but the third one, containing H^+, NH_4^+, NO_3^- and non-marine $SO_4^=$, is presumably of distant anthropogenic origin.

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