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Measurements of the chemical composition of cloudwater at a clean air site in central Scandinavia[1]

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ABSTRACT

A total of 179 samples of cloudwater were obtained during the summers of 1983 and 1984 at a clean-air site in the mountains of central Scandinavia. Impaction of droplets on teflon-coated wires provided samples with a time resolution of 5–30 min. Supporting data include cloud liquid water content, rainwater composition, aerosol number concentration, wind speed and direction, and 48-h isobaric trajectories.

Collected samples were analyzed for pH, Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, Cl^-, NO_3^-, and SO_4^{2-}. A wide range of concentrations were encountered, with, for example, sulfate concentrations ranging from 1 to 1600 μeq l^{-1}. Transport of air from remote regions (north Atlantic Ocean, Arctic) is shown to be associated with the very low concentrations, while the high concentrations occurred in conjunction with transport from industrial regions in Europe. Median clean-air concentrations in Arctic air, calculated from cloudwater composition and liquid water content, were 3 pptv ammonia (gas and aerosol combined), 6 pptv nitrate (gas and aerosol), and 30 ng m^{-3} sulfate.

1. Introduction

As awareness of the importance of clouds to atmospheric chemistry has increased, so has the amount of reported data on the chemical composition of cloudwater (see, e.g., Pruppacher et al., 1983). Studies of cloudwater composition to date have been concentrated on clouds in anthropogenically-influenced settings, with very little information available on the chemical composition of cloudwater in remote areas.

Ground-based collection of water from stratiform clouds, both raining and not raining, has been performed for approximately five weeks during each of the summers of 1983 and 1984 in the mountains of central Sweden. Clouds in very clean air from the north Atlantic Ocean were sampled on a number of occasions, while polluted clouds were less frequently encountered. In addition to providing samples for analysis of the dominant ions in cloudwater, the measurement programs have included supporting measurements of aerosol number concentration and cloud liquid water content.

The questions addressed by this study include: what are the concentrations of major ions in cloudwater in Sweden, how much do these concentrations vary, and what factors control the observed concentrations and their variability? Placed into a larger context, the goals of the study are to add to our understanding of the rôle of clouds in the cycling of substances through the atmosphere and the connection between the chemical composition of clear air (gases and particles) and the chemical composition of precipitation.

2. Methodology

The sampling site is located at an elevation of 1250 m asl on the Swedish peak Åreskutan

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(63°26′N, 13°6′E), about 70 m west of the upper terminus of an aerial tramway. The region around the site is sparsely populated, with the nearest population centers, Trondheim, Norway (pop. 134,000) and Östersund, Sweden (pop. 56,000) located 135 km west and 85 km southeast, respectively. A smelter located 60 km to the west is the nearest industrial site of consequence. With the exception of situations with westerly local winds, where the possibility of influence from the smelter plume must be evaluated on a case-by-case basis, measurements on Åreskutan are considered to be representative of air arriving over central Scandinavia. Contamination from activities at the tramway building are not considered to be a problem because easterly winds at the site were never encountered during the sampling periods. Further evidence of a lack of local contamination is provided by condensation nuclei measurements at the site, which do not exhibit the rapid, large fluctuations characteristic of local combustion sources. The site is located above the timberline, and the local surroundings consist of large rock outcroppings with scattered patches of moss and grass.

Samples of cloud water were obtained with a collector consisting of 0.45 mm diameter teflon-coated wires, strung at 3 mm intervals around the perimeters of two 25 cm diameter plastic disks, held 1 m apart by plastic rods (Falconer and Falconer, 1980). Stokes law analysis of the collection efficiency of this sampler indicates that cloud droplets of 10 μm diameter are collected with only 50% efficiency at wind speeds of 1 m s^{-1}, indicating poor performance of the collector at low wind speeds. For 80% of the cloudwater samples, the wind speed was greater than 5 m s^{-1}, yielding 50% collection diameters below 5 μm. Thus, the collector is considered to provide physically representative cloudwater samples under the conditions which prevailed during the sampling periods. The surface area of the collector is sufficient to provide a sample of 50 ml in 3–30 min, depending on the wind speed and cloud liquid water content.

Supporting measurements of wind speed, direction, and temperature were obtained both years. Samples of rain water were collected with polyethylene funnels and bottles. Measurements of cloud liquid water content were made only in 1984, using a heated-rod impactor operated at constant temperature (King et al., 1978). This sampler was equipped with a variable-area inlet controlled by the wind speed to provide near-isokinetic sampling conditions for wind speeds between 2 and 20 m s^{-1}, and was swivel mounted so that it always pointed into the wind. The detection limit of the instrument was 0.03 g m^{-3} and the accuracy of the technique has been reported to be 10–20% for the range of liquid water contents observed on Åreskutan (King et al., 1978). It is worth noting that the addition of this instrument to the sampling system requires the availability of electric power, thereby limiting the number of mountaintop sites where cloudwater measurements can be performed.

Concentrations of major ions in the samples of cloud and rain water were determined with ion chromatography (Na^+, NH_4^+, Cl^-, NO_3^-, and SO_4^{2-}), atomic absorption spectroscopy (Na^+, K^+, Mg^{2+}, Ca^{2+}), and glass electrodes (pH). Replicate pH and ion chromatographic determinations were made for all samples, and calibration standards (determined gravimetrically) were checked by comparison with a synthetic rainwater sample. Blank samples, obtained by spraying the sampler with distilled, deionized water, yielded median values for all species (except H^+) in the range 0.1–1 μeq l^{-1}. Ion balances for the 1983 samples could not be calculated due to the lack of NH_4^+ data. For the 1984 samples, the ratio of the sum of cations to the sum of anions was generally in the range 1.2–1.3, although wider variations were observed in the very clean samples. For such clean samples, the determination of H^+ (calculated as 10^{-pH}) is considered to contribute the greatest uncertainty to the ion balance, and an ionic imbalance of ca. 25% is not considered to be significant.

Receptor-oriented air trajectories arriving at the sampling site at 00 and 12 GMT were used to trace the movement of the sampled air during the three days preceding the sampling. The trajectories, kindly provided by the Norwegian Meteorological Institute, were isobaric and based on the 1000 mb geostrophic winds. The sampling days were grouped into categories according to the direction of the trajectories (cf. sectors in Fig. 1). Days when the trajectories lay in more than one sector were excluded. Similar trajectories, but based instead on independently derived wind fields, were obtained from the Swedish Meteoro-

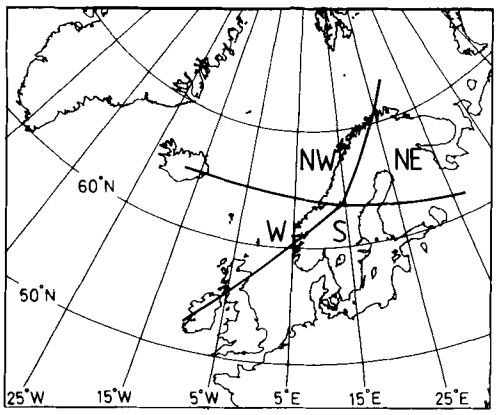

Fig. 1. Sectors used to classify air trajectories arriving at Åreskutan, Sweden.

logical and Hydrological Institute. In most cases, the trajectories from the two Institutes fell in the same category. Days when this was not the case were excluded from the analysis.

3. Results

A wide range of concentrations were encountered, as exemplified by the sulfate data reported in Table 1. Consistently low values were encountered in the northwest sector, where cloudwater sulfate concentrations were in the range 1–19 μeq l^{-1}, with a median value of 6 μeq l^{-1}. We believe that the minimum encountered value of 1 μeq l^{-1} is the lowest concentration ever reported for sulfate in cloudwater, and is comparable to the measurements of Neftel et al. (1985) for sulfate in the Greenland snowpack. The range of nitrate concentrations in the northwest sector, 0.4–6 μeq/l, with a median value of 2 μeq/l, is also comparable to the values reported by Neftel et al. (1985). Factors contributing to these extremely low values include the absence of major sulfur sources in the northwest sector (Semb, 1978) and the likely presence of strong removal processes upwind of the site on the Norwegian west coast.

Table 1. *Variability of sulfate in cloudwater*

		Concentration (μeq l^{-1})		
Sector	*N*	Minimum	Median	Maximum
NE	47	8	34	150
NW	41	1	6	19
W	33	4	30	220
S	4	660	700	930
ALL	179	1	19	1600

N: number of samples.
ALL: includes data that were not categorized in trajectory classes.

Cloudwater coming from the west and northeast sectors was also quite clean, although not as clean as that from the northwest. In contrast, on the one day when clouds were sampled in air coming from the southerly sector, cloudwater sulfate concentrations were roughly two orders of magnitude greater than those in clouds coming from the northwest. This difference is attributed to the presence of major sulfur sources in the southerly sector, the absence of such sources in the northwest, and possible differences in the removal histories of air parcels arriving from the two sectors. As seen in the example shown in Fig. 2, the air arriving from the southerly sector on 2 August 1983 had spent nearly 2 days over continental Europe before being rapidly transported to Åreskutan on the 3rd day. For comparison, the air masses arriving from the north on 24 and 25 July 1984 (Fig. 2) had median sulfate concentrations in cloudwater of 1.4 and 4 μeq l^{-1}, respectively.

Median cloudwater concentrations of all species for each sector are shown in Table 2. The pattern of sulfate concentrations seen in Table 1,

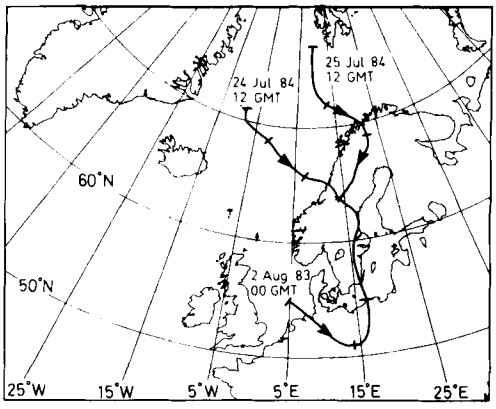

Fig. 2. Receptor-oriented trajectories arriving at Åreskutan on indicated dates. Each tick represents 24 h.

Table 2. *Sector median concentrations* ($\mu eq\ l^{-1}$)

Sector	N	H^+	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}
NE	47	33	17	7	<0.8	1	0.6	6	9	34
NW	41	13	0.5	<0.4	<0.8	<0.2	0.3	0.8	2	6
W	33	38	1	5	<0.8	0.6	0.8	4	10	30
S	4	370	N/A	33	6	12	22	19	68	700

N: number of samples.
N/A: not available.

with the highest concentrations in the southerly sector and the lowest concentrations in the northwesterly sector, is also evident in Table 2 for all other ions that were present at concentrations above the detection limit. Some interesting differences are apparent, however, differences which it is hoped that continuing measurements at the same site will be able to explain. Sea-salt concentrations, as represented by sodium and chloride, were surprisingly low in the northwest sector compared to the northeast. Although maritime air arriving from the northeast has spent a longer time over land, allowing more time for dry removal of sea-salt particles, air arriving at Åreskutan from the northwest may have encountered more vigorous wet removal processes along the west coast of Norway. The only samples from the program where sea-salt sulfate made a non-negligible contribution to the total sulfate concentration were associated with a northwesterly storm which caused hurricane-force winds at the site, and represent the effects of the generation of large quantities of sea-salt over the Atlantic Ocean.

Ammonium concentrations were markedly higher in air with trajectories from the northeast. A potential, local source of ammonia is venting of the sewage tanks at the tramway building located 70 m east of the measurement site. This does not appear to be the cause, however, as the local winds at the site were never from the east while samples were collected. A more plausible explanation is that ammonia emissions over land are stronger than over the ocean (Söderlund and Rosswall, 1982), resulting in higher concentrations in air arriving from the northeast.

Ratios of the concentrations of various species were investigated to see whether the different sectors had characteristic "signatures", that is to say, systematic differences from sector to sector in the relative abundances of the various species studied. The results, summarized in Table 3, are inconclusive because the day-to-day variations within a given sector (not shown) were as great as the sector-to-sector variations. If characteristic signatures exist, they are most likely to be found in species not measured as part of the present study (e.g., trace gases or metals).

The composition of clear air subsequent to cloud evaporation can be calculated from the measured cloudwater composition and liquid water content, assuming that equilibrium conditions determine the partitioning of a labile species between the cloud droplets and the gas phase surrounding the droplets. It is assumed that all aerosol mass is incorporated in the cloud droplets, which can lead to errors of order 10% even for water-soluble substances associated with 0.1–1 μm aerosol particles (Jensen and Charlson, 1985). The resulting quantity, termed the potential partial pressure (Daum et al., 1984), is reported in Table 4 for those cases where liquid water content measurements were made. For ease of comparison with other measurements, the ammonia and nitrate results are reported with gas-phase units (pptv) and the sulfate results with condensed-phase units (ng m^{-3}), even though no measurements were made of the partitioning of

Table 3. *Sector median concentration ratios*

Sector	N	$\frac{H^+}{\Sigma^-}$	$\frac{Cl^-}{\Sigma^-}$	$\frac{NO_3^-}{\Sigma^-}$	$\frac{SO_4^{2-}}{\Sigma^-}$	$\frac{NO_3^-}{SO_4^{2-}}$
NE	47	0.67	0.15	0.14	0.68	0.21
NW	41	1.6	0.10	0.21	0.67	0.31
W	33	0.82	0.07	0.24	0.66	0.34
S	4	0.49	0.02	0.09	0.89	0.10

N: number of samples.
Concentration ratios reported on an equivalent basis.

Table 4. *Potential partial pressures inferred from measured cloudwater composition and liquid water content (LWC)*

Date	Sector	N	LWC (g m^{-3})	NH_3 (pptv)	HNO_3 (pptv)	SO_4^{2-} (ng m^{-3})
24 July 1984	NW	5	0.19	1	5	14
25 July 1984	NW	1	0.16	4	5	38
28 July 1984	NE	2	0.07	14	8	31
29 July 1984	W	5	0.09	3	10	71
	ALL	23	0.16	3	6	33

N: number of samples.
1 ng m^{-3} SO_4^{2-} corresponds to 0.26 pptv sulfur.

these species between gas and condensed phases in clear air.

Very few measurements of sulfate, nitrate, and ammonia in summertime, Arctic air are available for comparison with the present study. Söderlund (1982) measured a total ammonia (gas plus particulate) concentration of 70 pptv during the Ymer-80 expedition in the remote, summertime Arctic. As part of the same expedition, Lannefors et al. (1983) reported a minimum sulfate concentration of 40 ng m^{-3}, while Pacyna and Ottar (1985) reported a range of sulfate concentrations on Spitsbergen for the month of August (1977–79, 1983) of 44–1100 ng m^{-3}. Not enough data are available to ascertain the cause of the much lower ammonia concentrations found in the present study. Considering the close agreement between the minimum summertime sulfate concentrations measured in the Arctic and on Åreskutan, it seems implausible to attribute the difference in the ammonia results to scavenging during transport to Sweden alone.

Total ammonia concentrations of $\sim$100 pptv have been reported for remote, maritime air in the southern hemisphere by Gras (1983). For total nitrate, Huebert (1980) reported concentrations over the remote, equatorial, Pacific Ocean in the range 30–140 pptv. The Åreskutan results are more than one order of magnitude lower than the equatorial and southern hemispheric results, a difference for which additional measurements are required in order to explain the causes.

The limited amount of liquid water content data prevents an unambiguous separation of the effects of physical and chemical processes on solute concentrations in the cloud water. Cloud physical processes determine the amount of liquid water available for dilution of the available solute, while chemical processes (e.g., source strength, transformations) determine the amount of solute. For example, sulfate concentrations observed on 12 July 1983 ranged from 300–1600 μeq l^{-1}; the nearly constant ratio of nitrate to sulfate (0.16) observed on this day provides an indication that much of the variation in concentrations was due to changing liquid water content rather than to differences in air composition. Visual observations on this day also indicate that liquid water concentrations were quite variable, with some samples taken in patchy clouds at the base of the cloud deck, and other samples taken in dense clouds with visibilities below 70 m. However, sulfate concentrations were observed to vary by a factor of 170 on 2 August 1983 while observed visibilities at the site remained in the range 10–100 meters, suggesting that changes in liquid water content were not as extreme as the observed changes in sulfate concentration. Thus, other factors must have contributed to the observed variations in cloudwater composition.

A time history of the measurements from 2 August 1983 is presented in Fig. 3, along with supporting meteorological data. The first few samples were associated with strong southerly winds, and had the highest concentrations observed that day. It began raining at 10:20, and by 10:50 the wind had shifted to the southwest. The weather map for this day (Fig. 4) indicates passage of a cold front in the morning, consistent with observations at the site. At 2 p.m. (local time), the front had moved some 200 km eastward and the site was located well into the cold air behind the front, with the flow direction being from the west and northwest. Clearly much of the

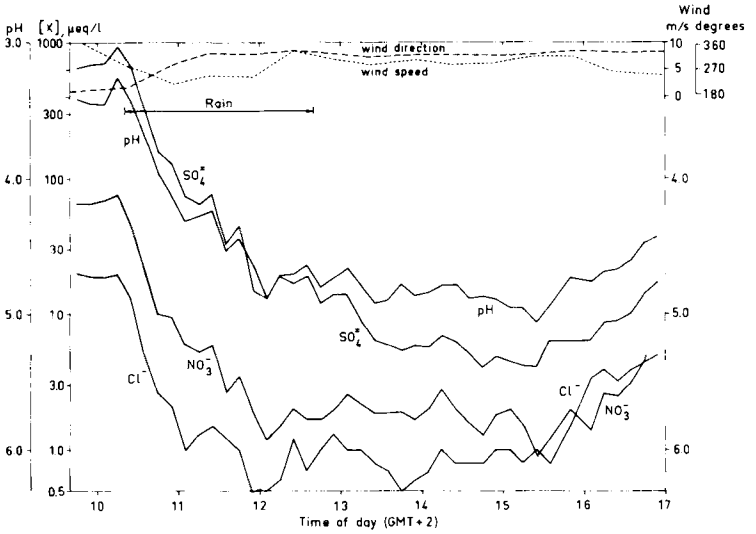

Fig. 3. Time series of cloudwater composition and meteorological variables observed on 2 August 1983 at Åreskutan, Sweden.

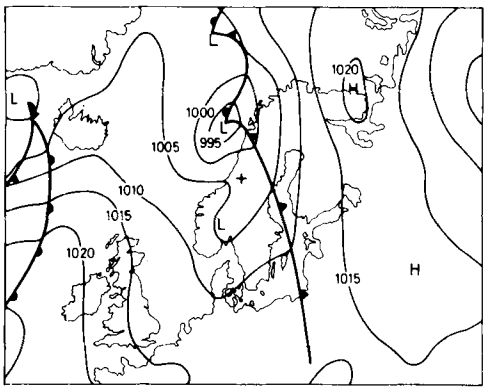

Fig. 4. Surface weather map on 2 August 1983 at 2 p.m. local time (12 GMT).

change from morning to afternoon in the chemical composition of the non-precipitating clouds is due to differences in air mass trajectory associated with the frontal passage. Further evidence of the difference in air masses is provided by the change in the median ratio of nitrate to sulfate from 0.10 before the front to 0.31 after frontal passage, and by the change in the median ratio of hydrogen to the sum of nitrate plus sulfate from 0.60 before the front to 1.8 after the front.

4. Conclusions

Long-range transport appears to be the major factor controlling the chemical composition of cloudwater at the sampling site in central Scandinavia. The influence of air mass origin is clearly seen in measurements made over a period of several hours during a frontal passage, where prefrontal air from the south had cloudwater sulfate concentrations over 200 times higher than postfrontal air arriving from the west and northwest.

Cloudwater composition measurements are seen to be a valuable tool for inferring the concentrations of some species in very clean, remote air. By taking advantage of the physical concentration effects of clouds, which typically accumulate the soluble material from 1 m^3 of air into less than 1 ml of cloudwater, concentrations down to the part per trillion level can be readily determined. Using this approach, cloudwater sulfate measurements in air masses arriving in Sweden from the Norwegian Sea are seen to be in good agreement with minimum sulfate aerosol concentrations observed in the European Arctic, while total (gas the particulate phases) ammonia and nitrate concentrations are a factor of ten or so lower on Åreskutan than in other remote, maritime locations for which data have been reported.

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