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Acidity of aerosol particles and of precipitation in the North Polar region and over the Atlantic

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ABSTRACT

During the Swedish polar expedition *Ymer-80*, measurements of the acid content of Aitken particles, of particles with radius between 0.1 and 1 μm, and of precipitation have been performed. Aitken particles were found to contain acid. The large particles also contain acid but may react neutral or alcaline in the case of an abundance in the radius range of sea salt particles produced by heavy weather conditions. The snow collected from the pack ice surface exhibited an acid reaction to a higher degree than could be explained from incorporation of condensation nuclei. The most plausible conclusion is that in polar regions, the precipitation is additionally acidified by uptake of gases. The results demonstrate that formation of acid in aerosol particles as well as in precipitation is to be considered a natural process in the undisturbed remote troposphere.

1. Introduction

The Swedish expedition *Ymer-80* in the arctic summer 1980 offered the opportunity to study the arctic aerosol in the polar region between northern Greenland and Franz-Josefs-Land. The arctic summer aerosol can be regarded as a real background aerosol as will be shown by the following considerations.

In the general circulation pattern of the earth, the circulation of the polar region is separated from the mid-latitude westerly circulation by the polar front. The polar front can be regarded as a zone of intensive mixing between temperate and polar air masses. Each mixing process in the lows developing at the polar front is accompanied by intense scavenging of trace substances. In summer, the mean position of the polar front is located far north; in winter it is shifted south. This picture can be inferred from the meridional and zonal distribution of heat and eddy fluxes (Newell et al., 1972). Newell's tables also imply that the mixing process is weaker in summer than in winter. Interpreting this picture with respect to the arctic aerosol, we may conclude that in summer the polar region is relatively well protected from anthropogenic influences, because the polar front lies north of the large emission sources of the industrialized countries, and because the mixing across the polar front is weak. In winter, the polar front moves southward, and part of the mid-latitude emission sources come to lie north of the polar front thereby emitting directly into the air of the polar cap without undergoing the intense scavenging process connected with the polar front (Carlson, 1981). Thus, there is a direct anthropogenic influence on the polar region during winter as is demonstrated, for example, by the winter maximum of aerosol bound vanadium found at Point Barrow (Rahn, 1981). On the other hand, the summer aerosols measured during the *Ymer-80* expedition can reasonably be interpreted as a real background aerosol without or with only a small anthropogenic component.

By a sophisticated comparison of trajectories and Aitken particle number concentrations, Jaenicke and Schütz (1982) demonstrated the existence of local anthropogenic sources within the Arctic. On the other hand, the particulate elemental carbon studies of Heintzenberg (1982) show that the mass fraction of strongly light absorbing material like soot is 10 times lower in summer than in winter aerosol. Since soot is a typical anthropogenic aerosol component, a low summer fraction

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of soot means little pollution of the Arctic in summer so that the arctic summer aerosol can be characterized as real background aerosol.

Another important aspect is the reduced contribution of sea salt to the aerosol in the pack ice region. In summer, sea salt production outside and transport into the pack ice region is comparatively small because of generally low wind speeds. Ocean water has a pH value slightly above 8. A reduced sea salt component in the aerosol can be expected to have an effect on the acid reaction of the particles. For this reason, aerosol measurements in the arctic summer may give some hints at the background aerosol of the troposphere.

2. Measurements

In clean arctic air, very low aerosol loads are expected so that one of the greatest problems was to avoid any ship contamination of the samples. A laboratory container was mounted in the front side of the ship ahead of the bridge. The vacuum pumps were installed in a separate pump house at the side of the laboratory container. The pump exhausts were fitted with filters to diminish artifical aerosol production near the collection place as much as possible. The aerosol was drawn through a suction tube from the container roof to the sampling device inside the container. The air intake was located at a height of about 16 m above the water surface. The sampling program of the air chemistry research groups was controlled by a very sensitive condensation nuclei counter which stopped the sampling when the nuclei number exceeded a preset level which usually was chosen about twice the ambient level. In this way, direct ship influence was avoided in almost all cases (Heintzenberg, 1982). However, it cannot totally be excluded that a very small ship influence remained which would cause a remarkable perturbation in cases of very clean air, for example when the Aitken nuclei level dropped as low as 10 particles/cm^3 or even below this value.

The Aitken nuclei were collected with a specially designed impactor. The aerosol is passed through an impactor nozzle, collecting the particles larger than 0.1 μm radius. The nozzle has a total length of 11 cm allowing collection at a rate of about 7 m^3 h^{-1}. The particles >0.1 μm are deposited on a slowly rotating, silicon oil coated cylinder. The rotation prevents overloading of the deposit because fresh silicon oil is permanently exposed to the nozzle providing for 100% collection efficiency. The remaining Aitken particles are deposited on a 28 cm^2 microsorban-filter (Delbag Company, FRG). The velocity at the filter surface is 0.7 m s^{-1}, yielding a particle retention of better than 95%, as was shown by tests. The filter consists of polystyrol fibers. The hydrophobic filters are washed several times before use by first making them hydrophilic with 1 ml of methanol. After washing, the filters are dried and stored in clean boxes until exposure. Blank tests showed that after washing, the pH value of the leaching solution was not affected by the filter material, while the electrical conductivity increased slightly. The sampling time was chosen so that the measuring signal of the electrical conductivity exceeded the blank value by a factor of at least 10. Due to the very low concentration of the Aitken particles, sampling took up to 4 days. A correlation with air mass or weather was therefore not attempted.

The amount of acid of the samples was determined by the following procedure. The filters were leached with 1 ml methanol and several ml (usually 4–6) of water; the electrical conductivity and the pH value of the solution were then measured. When the pH value was above 5, it was corrected for the influence of H^+ from dissociated H_2CO_3 originating from dissolved CO_2. Below pH = 5, H_2CO_3 is dissociated to such a small degree that a correction is not necessary. The non-H_2CO_3 H^+ ions are assumed to originate from strong acids; the total soluble material of the particles is calculated from the measured electrical conductivity, corrected for H^+, by assuming an average equivalent conductivity of 60 S cm^{-1} and an average equivalent weight of 35 g; then the relative fraction of acid contributing to the total soluble material can be estimated (Winkler 1980). In Figs. 2–4, this relative proportion is indicated by the inclined lines. A value of 10%, for example, means that 10% of the soluble material consists of strong acid. In Figs. 2 and 3, the average relation between the non-H^+ conductivity and the amount of soluble material is indicated by a second abscissa. All points were derived from the measurements and refer to a leaching solution of 0.4 ml H_2O per aerosol mass of 1 m^3 air. In a similar manner, we treated samples of the particles with 0.1 μm $< r <$ 1 μm which were collected on glass plates by a modified impactor designed by Jaenicke (1971).

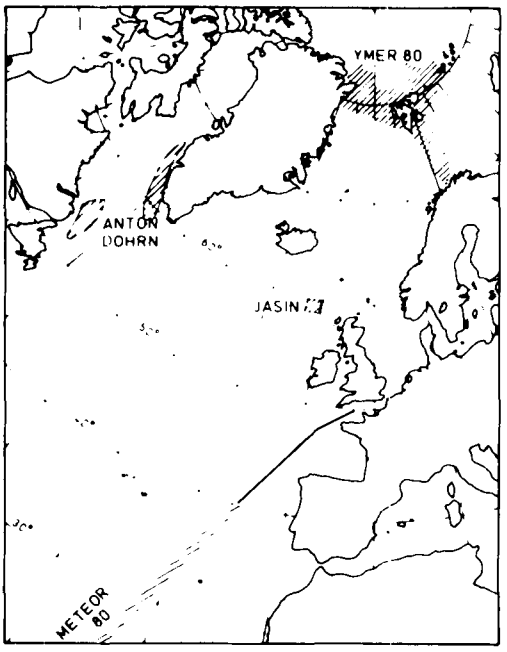

Fig. 1. Sampling locations from different expeditions. *Ymer 80*: region between northern Greenland and Franz Josefs Land; *Jasin*, RV *Meteor*: region west of Scotland; *Anton Dohrn*: region between Newfoundland and Western Greenland; *Meteor 80*: from Hamburg to Montevideo with samples collected between 30°N and 30°S.

In Fig. 1 the sampling locations are shown. During the *Ymer* expedition, particles were collected mainly in the region north of 78° N between northern Greenland and Franz-Josefs Land. For reasons of comparison, samples from other expeditions are also presented. Some samples are available from the *Jasin* area west of Scotland (60° N 12° W July through September 1978). A few data of inferior quality are available from a cruise of RV *Anton Dohrn* in the area between Newfoundland and Greenland during the late fall of 1980. The sampling on this cruise was only taken during headwind from a narrow sector. 5 samples have been collected during a *Meteor* cruise (1980) to Antarctica between 40° N and 20° S of the tropical Atlantic. Except for the *Jasin* samples, which were evaluated after the end of the cruise, all other samples were evaluated aboard directly after the collection had been completed.

Precipitation was collected during *Ymer-80* as snow from the pack ice snow cover, several 100 m upwind of the ship and several cm below the snow surface. During the *Anton Dohrn* cruise in 1980, precipitation was collected with a polyethylene funnel which was cleaned directly before sampling and exposed only during precipitation.

3. Results

The results are presented in pH-conductivity diagrams (Figs. 2–4) as explained above. In these diagrams, a pure diluted acid droplet has a fixed pH and electrical conductivity. Concentration or further dilution results in a shift parallel to the inclined 100% line, i.e. the soluble material contained in the droplet consists of 100% acid. At a given pH value, the electrical conductivity cannot decrease below a minimum value and vice versa so that there is a forbidden range where points of measurement are not permitted to occur. Additional dissolved neutral salts increase the electrical conductivity, but leave the pH unchanged. As mentioned above, the relative acid fraction can be read from the inclined lines. This relative fraction is not affected by the dilution or concentration of the leaching solution as far as no buffer mechanisms are active; it is therefore a good tool for judging the

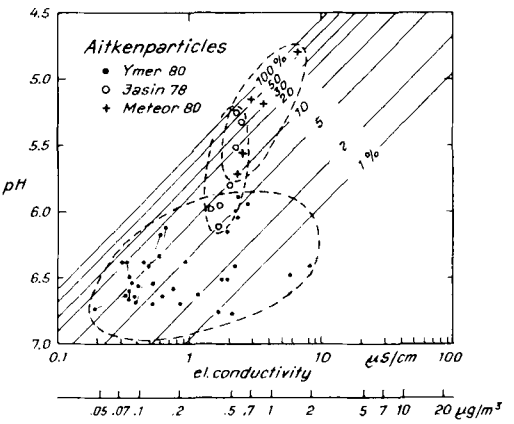

Fig. 2. Simultaneous measurements of pH values and electrical conductivities of Aitken particle leaching solutions. The data points are recalculated from the measured values in terms of particulate mass in 1 m^3 of air dissolved in 0.4 ml of water. The inclined lines indicate which fraction of the soluble material of the particles consists of acid. The second abscissa shows the average correspondence between electrical conductivity and concentration of soluble material in the air.

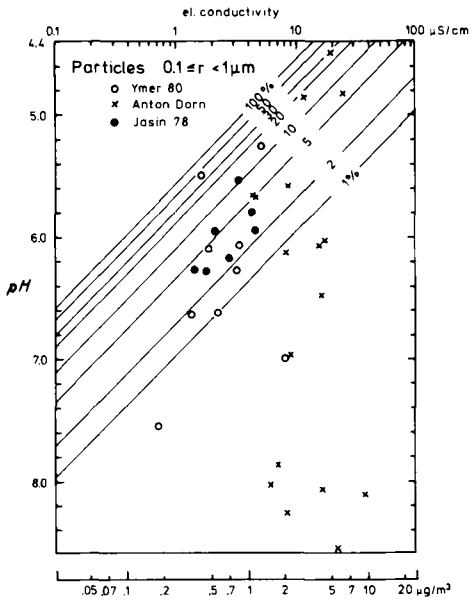

Fig. 3. Simultaneous measurements of pH values and electrical conductivities of leaching solutions for aerosol particles with radii between 0.1 and 1 μm. For further explanation see Fig. 2.

origin of the precipitation acidity as will be shown below.

Fig. 2 presents results for the Aitken particles. The 3 groups of values belong to 3 different regions. The lowest conductivities i.e. lowest total mass concentrations were found in the polar region. This is in accordance with the results of Jaenicke and Schütz (1982) who found that Aitken nuclei concentrations around or below 100 cm^{-3} are quite common in arctic air. The relative acid fractions varied from below 1% up to 20%. Multiple measurements are indicated by thin continuous lines between corresponding points in the figure and may serve to estimate the overall error of the measurements. There are differences due to uncertainties in the various parameters such as sampling volume, 50% cut-off radii of the impactor nozzles, pH and electrical conductivity measurements and filter blank values. The deviations perpendicular to the inclined lines demonstrate that the acid %s are accurate within 10%.

The Aitken particles from the *Jasin* area west of Scotland and from the tropical Atlantic (*Meteor 80*) show higher averages of the acid fractions than the arctic values.

The reason for the acid reaction of the marine Aitken particles is not well understood. We know, however, that the most abundant element of marine Aitken particles is sulfur, most probably in the form of SO_4 (Winkler, 1975), and that marine Aitken particles are produced out of the gas phase at least during sunshine (Haaf and Jaenicke, 1980). Therefore, the acid found in the Aitken particles can be assumed to exist in the form of H_2SO_4 or NH_4HSO_4. This assumption is confirmed by investigations of marine aerosol particles performed by Gravenhorst (1978) who found a rather complete compensation of the sum of $(H^+ + NH_4^+)$ by $SO_4^=$ in the particle size range $r < 0.45$ μm. His findings should also be valid for the Aitken particles ($r < 0.1$ μm) under investigation here. Besides sulfur, carbon can also reach high concentrations in the marine Aitken particle range (Schütz et al., 1978). Furthermore, organic acids may be produced from decomposing dead organic matter by gas to particle conversion. However, the high carbon concentrations reported by Schütz et al. (1978) were measured during weather situations when the coastal sampling station was land influenced (Schütz, private communication). Although we cannot exclude carbonic acids, they do not seem to play a major role in the marine atmosphere. In summary, we can conclude that the marine Aitken particles contain considerable amounts of free acid even in an undisturbed polar environment.

The results for the large-particle range is depicted in Fig. 3. Large amounts of acid were found but there were also samples reacting neutral or alcaline. During the *Anton Dohrn* cruise between Newfoundland and western Greenland, most samples reacted neutral or alcaline. In the large particle range, the influence of sea salt becomes remarkable. Sea water has a pH of around 8.2, and the sea salt particles consequently react alcaline. Although the mass of the sea salt is concentrated in particles >1 μm radius, there is a minor sea salt fraction in the particle size range below 1 μm radius, the amount of which depends on the weather conditions, mainly on wind speed.

In the pack ice covered region and during the *Jasin* cruise where aerosol was collected under calm summer conditions, sea salt influence was small compared to samples from the *Anton Dohrn* cruise during the late autumn with high sea salt production. Barrie et al. (1981) who studied the

chemical composition of winter aerosol in the high Canadian arctic, found H_2SO_4 to comprise approximately 30% of the total mass. Heintzenberg et al. (1981) also concluded from measurements in Spitzbergen, that the winter aerosol must be highly acidic. Our measurements indicate %s ranging from less than 1% to 40%, most values being below 15%. The lower values found in summer may be caused by neutralization due to NH_3, the production of which is increased during the arctic summer. Our results provide additional information showing that the arctic large aerosol particles contain appreciable amounts of acid throughout the year.

Besides the aerosol, snow samples were investigated in order to find out whether the amount of aerosol acid is large enough to explain the acid content of the precipitation. Fig. 4 shows the measurements.

All samples from *Ymer* were collected north of 80° N. In the pack ice snow, pH values as low as 4.7 occurred. Furthermore, high acid fractions between 10 and 20% were frequently observed. Likewise, near Newfoundland, pH values of 4.8 have been measured but there the acid fractions remain below 5%. In this region, the acid fractions are obviously lowered due to the large influence of sea salt as proven by the generally high electrical conductivities of the precipitation. Koerner and Fisher (1982) reported on measurements of ice cores from northern Ellesmere island (81° N) in Canada. Their average values for the last 25 years are also included in Fig. 4 and again indicate high acid fractions between 30 and 50% of the total soluble material. For comparison, some results are shown from measurements in Antarctica, one point from the station Dome C (Legrand, 1980) and two points from James Ross island (Aristarain, 1980). The relative acid fractions of both stations are comparable to those of the pack ice snow, or even slightly higher due to a still more reduced sea salt influence. Cunningham and Zoller (1981) concluded that aerosol from South Pole station in Antarctica mainly consists of sulfate. Their findings, combined with the high acid fractions found in the antarctic snow, (Aristarain, 1980, Legrand, 1980) imply that H_2SO_4 is the main acidifying component. Indeed, Delmas and Aristarain (1981) found a good correlation between H^+ and excess $SO_4^=$ (non sea salt $SO_4^=$) in the antarctic snow. This process seems to be of importance in both polar regions.

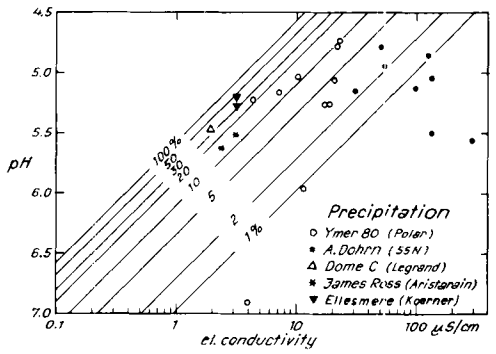

Fig. 4. Simultaneous measurements of pH values and electrical conductivities of molten snow on precipitation. The symbols Δ, ▼, *, refer to literature data from the Arctic and from Antarctica. For further explanation see Fig. 2.

To find out how much snow acidity presumably originates from the aerosol particles, suitable mean values have to be computed. Since we are interested in only relative fractions of acid, average pH values may be computed by normalizing the electrical conductivity to 10 μS cm^{-1} without loss of generality. In the pH-conductivity diagram, this procedure corresponds to a movement parallel to the inclined lines; in practice, it means the dilution or concentration, respectively, of the precipitation water or aerosol solution until an electrical conductivity of 10 μS cm^{-1} is reached. The relative amounts of free acid do not change by this method. The following average pH values for the arctic (*Ymer*) aerosol and precipitation are obtained:

precipitation	5.12 pH,	12% free acid;
Aitken particles	5.4 pH,	5% free acid;
particles >.1 μm	5.8 pH,	3% free acid.

We see that the precipitation reacts slightly more acid than the condensation nuclei. If we additionally saturate the aerosol solution with CO_2 in order to simulate the precipitation process, there still remains a small pH difference between precipitation and aerosols. We can therefore conclude from observational evidence, that the snow in arctic regions is acidified not only by aerosol particles but also by acidifying gases. That the precipitation in remote areas has a lower pH than the equilibrium CO_2 values, was also concluded by Charlson and Rodhe (1982) from budget considerations which allow for pH values well below 5. Whether the

acidifying gases are taken up during the precipitation process or by dry deposition of these gases into fallen snow, cannot be decided on the basis of our measurements. Evaporation of fallen snow does not lead to increasing acidity because it would lower the pH but not increase the relative amount of free acid.

4. Conclusion

During summer, the arctic aerosol can be regarded as rather undisturbed background aerosol. We have shown that Aitken particles contain acid fractions of the total soluble material up to 20%. Particles with radii between 0.1 and 1 μm usually react acid in the pack ice region or over the open sea, as long as the sea salt fraction in this radius range is small. Acid fractions up to 40% of the soluble matter were measured. Comparison with precipitation samples showed that the average aerosol acidity does not fully account for the precipitation acidity. In precipitation, pH values as low as 4.75 have been found in the geographical region north of 80° N. The measurements have demonstrated that in the clean arctic summer atmosphere which is practically free of anthropogenic influence, formation of acid is to be considered a natural process.

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