# Coastal Antarctic aerosol and snowfall chemistry

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**Abstract.** Aerosol samples have been collected at three stations on the coast of Antarctica. At Dumont d'Urville Station, samples have been collected for 4 years, at Halley Station for 2 years, and at Neumayer Station for 12 years. Fresh snow samples have also been collected at the three sites. At Halley, daily surface snow samples were taken, as well as firn cores covering the sampling period. Meteorological (including upper air) data are available at the three sites. In the subsequent papers of this special section, the data from the three stations have been combined in order to make general statements about the chemistry of aerosol in coastal Antarctica, about the differences between sectors of Antarctica, and about the relationship between air concentrations and the chemistry that is eventually seen in ice cores. This paper summarizes the samples collected and the sampling methods used at the three sites. It also highlights the main role of each paper in this special section.

## 1. Introduction

The chemical content and chemistry of the atmosphere above Antarctica is of considerable interest for a number of reasons. It is undoubtedly the cleanest part of the Earth's troposphere and therefore offers, for some situations, the chance to study natural conditions that may have prevailed elsewhere in preindustrial times. Its unique conditions of temperature and of day/night represent a natural laboratory to study important atmospheric chemical transformations. An additional reason for studying the Antarctic atmosphere, and one which played a large part in prompting the studies described in this special section, is the need to interpret ice cores. Ice core records are used to determine past variations in atmospheric composition that may be due to anthropogenic or climatic change or to natural variability. For relatively long-lived trace gases, such as carbon dioxide and methane, good atmospheric measurements exist from the Antarctic, and the ice core records are rather well understood in terms of atmospheric concentrations. However, for short-lived species (aerosol particulates and some gases), the situation is much less clear. Understanding of ice core records for such species is currently inhibited by our very limited knowledge of the Antarctic atmosphere in the present, and of the processes of air to snow transfer [Bales and Wolff, 1995; Wolff and Bales, 1996].

Although the Antarctic stratosphere has now been explored in some detail because of the ozone depletion phenomenon, the troposphere remains very little studied. In central Antarctica, only one station, South Pole, has seen any significant chemical measurements [Bodhaine, 1996], and even there a continuous and detailed record of the major aerosol components (that are generally

most studied in ice cores) is lacking. Considering that there are currently in progress or planned at least four major deep ice cores in central Antarctica, this is a crucial deficiency.

In coastal Antarctica, because of the presence of more manned stations, the situation is slightly better [Wagenbach, 1996]. Continuous, ongoing records of aerosol species and some other air chemistry are available for Neumayer since 1983 [Wagenbach et al., 1988] and for Mawson since 1989 [Prospero et al., 1991; Savoie et al., 1992], and some shorter time series are available for two stations on the Antarctic Peninsula [Savoie et al., 1993]. However, this still represents a very poor distribution of data for such a large continent, and this makes it hard to confirm findings, or to separate out findings that apply to coastal Antarctica as a whole from those that are specific to a small region.

With this in mind, and motivated specifically by the need to improve interpretation of ice core records they had obtained [e.g., Legrand and Delmas, 1988; Mulvaney and Peel, 1988; Legrand et al., 1992; Mulvaney et al., 1992; Minikin et al., 1994; Wagenbach et al., 1994], scientists from France, Germany, and the United Kingdom initiated in 1991 a collaborative project to study the aerosol and snow chemistry at three coastal Antarctic stations. The project was funded by the funding agencies of the three groups and by the European Community, and the papers in this special section are the result of the work carried out.

Specifically, continuous aerosol sampling was carried out at Neumayer, where it represented an enhancement of the existing program, and at Dumont d'Urville and Halley, where new programs were set up (Figure 1). Sampling was carried out at different intervals at the three stations, and the details are described below and in the papers that follow. Sampling of fresh snow and of surface snow was also carried out at the three stations. Full synoptic meteorological data (including upper air data) were available at each station [König-Langlo et al., this issue]. Two of the three stations are located on ice shelves and are (in the context of the continent) rather close to each other in the Atlantic Ocean
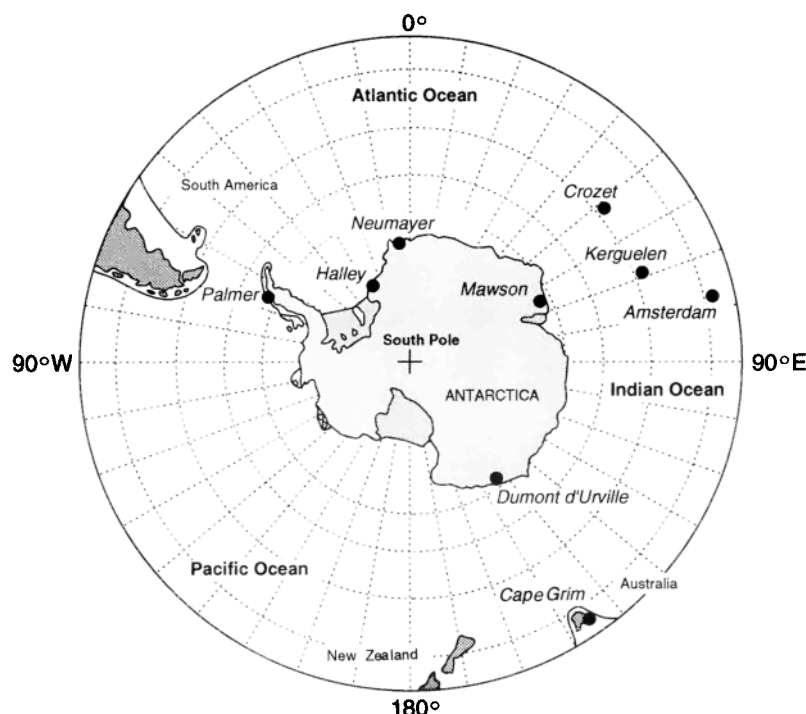
**Figure 1.** Map of Antarctica, showing the three stations and other sampling sites mentioned in the accompanying papers.

sector. The third (Dumont d'Urville) provides a contrast, being situated on an island in the Pacific Ocean sector.

The remainder of this paper describes the sampling program at each station and then briefly summarizes the content of the papers that follow. These have been arranged according to atmospheric chemical interest rather than according to the sampling site, in order to draw the widest possible conclusions about coastal Antarctic aerosol and associated snow chemistry.

## 2. Sampling Sites and Procedures

### 2.1. Dumont d'Urville

The French station at Dumont d'Urville (66°40'S, 140°01'E) faces the Pacific Ocean (Figure 1). It is sited on a small island (900 m x 500 m maximum dimensions), Ile des Pétrels, about 1 km from the Antarctic mainland (Figure 2). The island is one of about 60 isles and islets in the Pointe Géologie archipelago. The dominant wind is the katabatic flowing from the continent; the main meterological parameters are discussed elsewhere [König-Langlo et al., this issue]. The island is about 50% ice-covered, with the remainder consisting of metamorphic rocks with some permafrost zones. Some additional measurements were made on another island, Ile du Gouverneur, about 3 km WSW from Ile des Pétrels.

The station consists of about 60 buildings and shelters, some of which are used only in summer. Because of its situation, it is impossible to define a truly "clean" sector, such as that defined at South Pole and Neumayer. The choice of sampling sites was a compromise between a clean location (away from station activities) and the need for year-round access despite the harsh conditions. The main site for aerosol collections was the "Hall Fusée," situated upwind of all the station buildings. The disadvantage of this site was that in winter access sometimes became difficult and dangerous. For this reason, a second site (used for both aerosol

sampling and for gas-phase sampling) was set up at "Labo 3," which is downwind of some buildings, and is within 100 m of most of the main station buildings. A third site, using solar panels to produce power was set up for January and February 1994 at Ile du Gouverneur, in order to test the possibility that contamination had affected the samples from the other two sites.
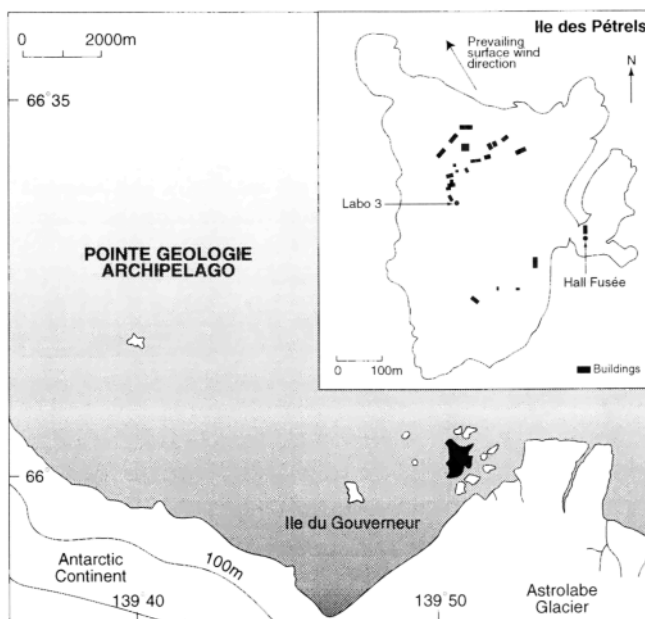


**Figure 2.** Map of local area around Dumont d'Urville indicating the location of the three sampling stations, Hall Fusée, Labo 3, and Ile du Gouverneur.

At each site, the sampling system consisted of a vacuum pump upstream of a volume meter, a manometer, and PVC tubing leading to the sampling head. At the head, the filter holder was mounted on a short mast, 2 m high, surrounded by a cylindrical stainless steel shield to protect the filter from direct deposition of sea salt. For aerosol sampling, the filters used were Gelman Zefluor (PTFE) 47 mm diameter, 0.4 µm pore size filters. Gas-phase measurements for acidic gases and for ammonia were also made at "Labo 3" using nylon filters, denuder tubes and mist chambers [Legrand et al., this issue; Wagenbach et al., this issue (b)].

For the aerosol sampling, flow rates were 3-4 m$^3$ h$^{-1}$. The sampling interval was planned to be 1 day in summer and 2 days in winter. Bad weather sometimes increased these intervals, in general up to 2-3 days, and on rare occasions even to a week. The amount of air sampled on each filter ranged from 70 to over 500 m$^3$. The data sets used in the special section include some data from both the "Labo 3" site and the "Hall Fusée" site. Sampling began in January 1991, and data are available until April 1996. The main sampling details are shown in Table 1.

A comparison was made of samples collected simultaneously at the three sampling sites to establish the effect of emissions of pollutants from the stations. For the marine elements, there was no significant difference in the Cl$^-$/Na ratio between the three sites, and higher concentrations at Ile du Gouverneur could be explained by its location on a smaller island, with more seawater near the sampling site. For sulphate and nitrate, there was generally good agreement, but some filters that were visibly grey (indicating contamination from combustion at the station) had somewhat elevated concentrations of sulphate and, to a lesser extent, nitrate. This problem was dealt with by identifying all filters showing signs of coloration. These were compared with "clean" filters collected simultaneously, or just before or after the same period. As a result, about 20 values (mainly from "Labo 3") have been eliminated from the data set. For a final set of ions, notably ammonium, higher concentrations were regularly found at "Labo 3" than at "Hall Fusée," and at "Hall Fusée" than at Ile Gouverneur. This was due to the proximity of penguins at the sampling site and is discussed in the paper on ammonium [Legrand et al., this issue].

Filters were assembled onto their supports at Dumont d'Urville under a laminar flow hood taking all usual precautions against contamination, and the complete filter holders were transported to and from the sampling site in a polyethylene bag. The filter holder was rinsed three times in ultrapure water between uses, and the

cleanliness of the procedure was checked approximately every 10 samples with a field blank that was mounted onto a filter holder and had air pumped through it for 10 s. Filters were stored before analysis in polystyrene cuvettes covered with Parafilm, kept in polyethylene bags.

Filters were extracted in 1 mL of methanol (to aid wetting of the filter) plus 9 mL of ultrapure water. The containers were lightly agitated to improve extraction. Samples were analyzed for anions and cations by ion chromatography after filtration through a 0.4 µm Nuclepore filter. After the first extraction, some filters were extracted a second time to estimate the extraction efficiency. The concentrations seen in the second extraction can be explained by the approximately 100 µL of water left in the filter, implying an approximately 100% extraction efficiency. The blanks for methanol, the extraction procedure, and the filters were measured, as well as the field blank. They will be discussed as appropriate in the later papers, but in each case the field blank was insignificant compared to typical sample values, so no correction was made for it. The analytical procedure on the ion chromatograph, and the precision of the data obtained, will be discussed for each ion in the appropriate paper.

After each snowfall, two to four surface snow samples were collected and analyzed. As at all the stations, it was difficult to differentiate between snowfall and blowing snow, although the continual strong winds at Dumont d'Urville make it particularly difficult. Very high concentrations of marine ions may indicate some direct deposition of sea salt on the snow surface. The snow samples will be discussed further in a paper on air-snow transfer [Wolff et al., this issue].

## 2.2. Halley

The United Kingdom station at Halley faces the Atlantic Ocean (Figure 1). It is situated on the Brunt Ice Shelf, just 32 m above sea level. The station has been moved periodically, and re-built, and the aerosol sampling took place at two nearby locations. Aerosol samples from February 1991 to late January 1992 were collected at the Halley 4 station (75°36'S, 26°48'W), while aerosol samples from February 1992 to the end of January 1993 were collected at Halley 5 station (75°35'S, 26°19'W), about 14 km distant (Figure 3). The station moves westward with the ice shelf at approximately 760 m yr$^{-1}$. The topography around the station is very flat up to the grounding line about 40 km southeast of the station, where the ice rises steeply into the Coats Land plateau.

**Table 1.** Main Characteristics of Sample Sites

|  | Dumont d'Urville | Halley | Neumayer |
|---|---|---|---|
| Location | 66°40'S, 140°01'E | 75°36'S, 26°48'W<br>75°35'S, 26°19'W | 70°37'S, 8°22'W |
| Sector | Pacific | Atlantic | Atlantic |
| Topography | small island | flat ice shelf | flat ice shelf |
| Distance to water | <300 m | 15 km | 6.5 km |
| Sampling periods | 1-7 days | 1-2 days | Up to 3 weeks |
| Data available | Jan. 1991 to April 1996 | Feb. 1991 to Feb. 1993 | March 1983 to Feb. 1996 |
| Aerosol filter type | teflon<br>low volume | mixed cellulose<br>low volume | cellulose, 24 cm<br>high-volume |
| Snow samples available | fresh snow | daily surface snow<br>snow accumulations<br>firn cores | fresh snow when low<br>wind speed |
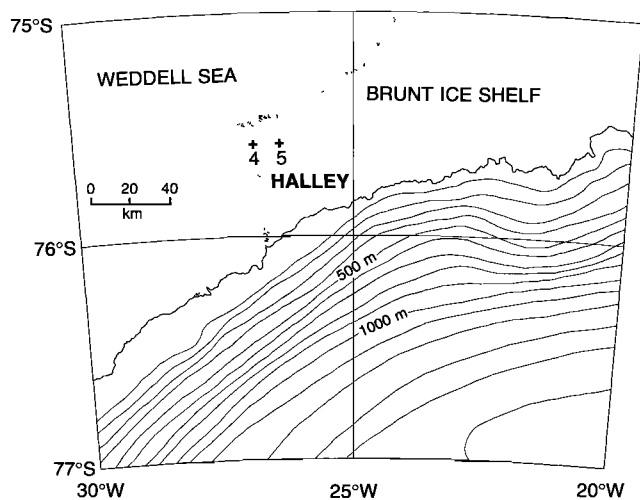
**Figure 3.** Map of local area around Halley showing the positions of the Halley 4 and Halley 5 stations on the Brunt Ice Shelf.

There is no vegetation or exposed rock within 200 km, and the nearest wildlife is an emperor penguin colony about 15 km away.

The ice front is some 15 to 30 km from the station in directions from about 200° to about 45°. During summer months, a lead, which may be several tens of kilometers wide, extends along the ice front. During the winter, the Weddell Sea becomes ice-covered, and fast ice forms along the ice front. However, the prevailing easterlies keep open a number of polynyas where the ice front has a north-south orientation. These tend to close up when the easterlies are temporarily replaced by westerlies, but sufficient open water still remains for the polynyas to be a significant local water vapor source. The favored surface wind direction is from the east (over 60% in 45°-135° sector), but westerly wind directions are also common [King, 1989]. The main meteorological parameters are discussed elsewhere [König-Langlo et al., this issue].

The penguin colony on fast ice about 15 km northwest of the station is estimated to contain about 50,000 adult birds. They start to arrive in June and generally disperse along the coast by late December. A second smaller colony has been recorded on fast ice southwest of the station.

At Halley 4, the main station buildings were under the snow surface, but several smaller huts, and the generator chimneys, were aboveground. The aerosol sampling pump was located in a small hut 300 m SE of the station generators. This is a direction that is almost constantly upwind of the generators and most other station activities. The sampling head was a further 10 m from the hut. At Halley 5, the station buildings are aboveground, on jackable legs, and there are two separate generators. The sampling pump was located in a building 300 m from the two buildings with generators, in a direction that is commonly upwind of both buildings. The sampling head was again about 10 m from the building containing the pump, in a designated clean sector from which vehicle and other activity were excluded.

In the case of Halley 5, the existence of two generators at some distance apart made it impossible to find a direction that is almost always upwind of generators, and it is clear that generator exhaust sometimes passes near the filter inlet. However, comparison of aerosol records with black carbon data collected in an adjacent location [Wolff and Cachier, this issue] shows that there is no significant contamination for methane sulfonic acid (MSA), sulphate or sea-salt species, even during major events of black carbon contamination from the station.

At both sites, the sampling system consisted of a vacuum pump exhausted through a flow meter and a gas volume meter. Silicone rubber tubing connected the pump to the sampling head. At the head, the filter holder was mounted, open-face downward, inside an upturned polyethylene jar intended to prevent blowing snow blocking the filter. The jar was mounted at about 2 m height on a nylon pole and was free to swing slightly in the wind, aiding the removal of snow and rime. The filter holders were 37 mm polystyrene filter monitors, with a porous polyethylene support pad. Filters were mixed cellulose ester (Nuclepore MF) 37 mm diameter, 0.8 μm pore size. The manufacturers suggest that this type of filter collects >99.99% of aerosol particles.

Aerosol sampling flow rates were approximately 1-2 $m^3$ $h^{-1}$. The sampling interval was planned to be daily, but bad weather occasionally increased the interval to 2 or (rarely) more days. The amount of air sampled on each filter was therefore mainly in the range 20-60 $m^3$. Combining the data from the two Halley stations, data are available from February 1991 to February 1993.

Filters, support pads, and monitors were all cleaned and assembled in Cambridge (United Kingdom) before transport to Antarctica. Filters were cleaned in batches of 25 with several successive batches of ultrapure water over a period of 1-2 days, including a short time in an ultrasonic bath. They were then dried on their support pads in the air flow of a Class 100 clean laboratory. After assembly into closed monitors, the entire monitor was sealed into two layers of rinsed plastic bags and transported to Antarctica. When required, operators at Halley, wearing long polyethylene gloves, opened the bags, removed one monitor cap, and attached the filter to a sampling head. They then opened the monitor (to give open-faced sampling). At the end of sampling, they simply reversed this procedure, which minimized handling. Used filters were returned to the United Kingdom in a freezer at -20°C, and kept frozen until just before extraction took place. Field blanks were collected at regular intervals by placing a filter on the head, pumping for a few seconds, then leaving it without pumping for 24 hours. It must be noted that there were generally between 3 and 15 months between filter cleaning and usage, and a period of 1-3 years between filter usage and extraction/analysis.

Filters were extracted in 8 mL of ultrapure water in a Class 100 clean laboratory, using an ultrasonic bath to aid extraction. Samples were analyzed (also in a clean laboratory) for anions by ion chromatography, and for cations by atomic absorption spectrometry (or ion chromatography in a few cases, including some where ammonium was determined). Cation analyses are only available for the Halley 4 samples at present. After the first extraction, some filters were extracted a second time to estimate the extraction efficiency. The concentrations seen for chloride and sulphate can be explained by the approximately 0.5 mL of water left in the filter, implying an extraction efficiency close to 100%. For MSA, there is some limited evidence for a lower extraction efficiency (perhaps as low as 80%). However, in the absence of strong evidence or an explanation, we have made no correction in our data set, but it should be remembered that this means that the possibility exists that the Halley MSA data are consistently up to 20% below the true values.

Although our filter cleaning method was highly successful in reducing the concentrations of ions on the filters when carried out on individual filters, it was somewhat less successful on the batches used to clean the large number of filters in this study. Consequently, the field blank, due mainly to the filters themselves, was significant for all ions and has been removed from the concentrations in the data set. The variability of the field blank was large enough that some negative numbers appear in the data set. This reflects the relatively poor detection limit with the low air volumes and high field blanks at Halley. The analytical method

and the value of the detection limit for each ion is discussed in each appropriate paper. The field blanks for nitrate were particularly high, with variability so large that the data for nitrate at Halley could not be used in the relevant paper [*Wagenbach et al.*, this issue (b)]. Tests suggest that the cleaned filters probably did not have this high nitrate content, but that uptake occurred during drying (when the filters may have been inadvertently exposed to the fumes from some nitric acid cleaning baths) and/or the long storage time.

Samples of the snow surface and of fresh snow accumulations were also collected at Halley 4 station from July 1990 to February 1992. Data are also available for cations from collections made at Halley 5 later in 1992. The snow sampling sites were located near to the aerosol sampling sites, in areas free of vehicle activity. Weather permitting, two samples (one only during 1990) of surface snow were collected into 9 mL polyethylene bottles each day, irrespective of whether there had been any change to the snow surface. The bottles had been cleaned in baths of ultrapure water before dispatch to the Antarctic in sealed polyethylene bags and were transported back to the United Kingdom frozen. The sampling tool consisted of a specially designed holder with two aluminium runners and two bottle holders between the runners. When the runners were slid over the surface, the bottles would collect the snow at a depth of 0-10 mm, and 3-15 mm, respectively. Naturally undulating surfaces will have varied these depths somewhat, but both samples will have collected a skin of approximately 1 cm. The operators, wearing clean gloves and hood, would move to a fresh patch of snow upwind of the previous one each day. On days when a significant accumulation of snow occurred (which could have been snowfall or drift), another sampler was used to collect the accumulated snow into precleaned 30 mL bottles. This sampler allowed a vertical section of up to 12 samples to be collected, depending on the amount of accumulated snow.

In the laboratory at Cambridge, samples were melted and analyzed for anions by ion-chromatography, and for cations by atomic absorption spectrometry. The procedural blank (bottle taken through the whole procedure, then filled with ultrapure water) was close to the small analytical blank. The analytical procedure and blanks will be discussed in the appropriate papers [*Mulvaney et al.*, this issue; *Wolff et al.*, this issue].

At Halley 5, an aethalometer measuring black carbon in the atmosphere was deployed from February 1992, with data available until the end of 1995. The sampling head was located next to the aerosol filter inlets. The method will be discussed in detail in the paper on black carbon [*Wolff and Cachier*, this issue].

### 2.3. Neumayer

The German station at Neumayer is situated at 42 m above sea level on the Ekström Ice Shelf, facing the Atlantic Ocean (Figure 1). The station position was moved by 7 km in March 1992, from 70°37'S, 8°22'W to 70°39'S, 8°15'W. The ice shelf edge is located 6.5 km from the station to the east (Figure 4). Atka Bay is mostly covered with fast ice, and apart from some small tide cracks, no open water exists. Only during January and February does Atka Bay become mainly ice free. In the Weddell Sea, 15 km north of the station, pack ice is predominant. In some years, this vanishes completely for a few weeks in summer, while some ice floes remain in other years. Strong westerlies and winds with a significant offshore component can open a coastal polynya north of Neumayer in any season.

There is no vegetation or exposed rock in the vicinity. An emperor penguin colony is situated about 7 km east of the old station (6 km northeast of the new station). Adelie penguins also occasionally visit the station when Atka Bay is ice free. The dominant surface wind direction is easterly, though other directions also occur. The main meteorological parameters are discussed elsewhere [*König-Langlo et al.*, this issue].
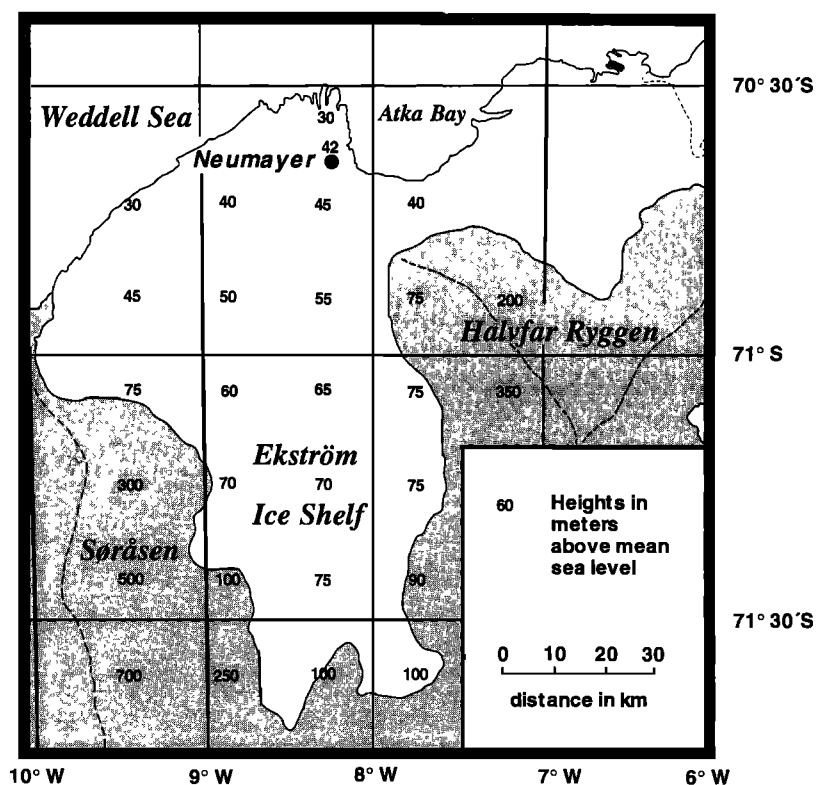


**Figure 4.** Map of local area around Neumayer on the Ekström Ice shelf.

Power for Neumayer is provided by diesel generators at the main station, so that exhaust gas emissions are concentrated there. Sampling for aerosol and other measurements was carried out at a clean air chemistry laboratory situated 1500 m south of the main station. Northerly winds are hardly ever observed, so that only vehicle emissions could have any effect on air chemistry measurements. Sample collection techniques have been described before [Wagenbach et al., 1988]. Briefly, air was collected through a ventilated stack 7 m above the snow surface. This was intended to reduce problems due to the extensive blowing snow at the site. To further minimize any chance of contamination from the station, sampling was automatically interrupted if preset levels of local condensation nucleus concentration, wind speed, or wind direction were reached.

The main sampling system was a high-volume system with a flow rate of 150 m³ h⁻¹. Samples were collected on a pair (in series) of Whatman 541 cellulose filters (24 cm diameter). The sampling period was varied through the year, but could be up to 3 weeks, giving a sample volume of between 10,000 and 50,000 m³, considerably higher than that used at either of the other two stations, but a lower time resolution than at the other sites. Sampling began in 1983, and data are available until the start of 1996.

Filters and double polyethylene bags to contain them were cleaned prior to shipment to Antarctica by successive soaks in isopropyl alcohol, dilute $HNO_3$ and HF, and ultrapure water over a period of about 2 weeks. Parts of each filter were analyzed after transport to Heidelberg for MSA and major anions by ion chromatography. Extraction was carried out by soaking the filter in ultrapure water for 40 min in an ultrasonic bath. Beforehand, $^7Be$ and $^{210}Pb$ activities were measured on each filter nondestructively (by gamma spectroscopy), and $^{10}Be$ was measured on filter aliquots. Analysis for these radioisotopes of first and second filters showed a collection efficiency of 84% on the first filter. Field blanks, placed in the filter holder in the field for one day, gave a blank for all ions which is negligible compared to the large amounts on each filter after the sampling period. A fuller description of the methods used has been given elsewhere [Wagenbach et al., 1988], and the analytical method will also be discussed in the relevant papers.

Occasional samples of freshly fallen snow were collected at Neumayer under low wind conditions. These will be discussed in the appropriate papers [Mulvaney et al., this issue; Wolff et al., this issue].

## 3. Role of Papers in Special Section

In the papers that follow in this special section, data from all three stations have been combined to allow discussion of factors that are common to coastal Antarctic sites and those that are specific to each site. In some papers, the higher (daily) resolution of the Halley samples and the detailed daily snow collections there have been used to look at processes in more detail. In other papers, the longer records at Dumont d'Urville and especially at Neumayer are used to advantage and give greater confidence in conclusions about seasonal trends in particular.

In order to provide the crucial meteorological setting for the remaining papers, a paper comparing the surface and upper air climatology has been included [König-Langlo et al., this issue]. This shows particularly the contrast between Dumont d'Urville, dominated by the outward flowing katabatic winds, and the other stations, which are more influenced by cyclonic activities. Dumont d'Urville is also near the edge of the stratospheric vortex, while the other stations are more firmly within it. A second meteorological paper [Kottmeier and Fay, this issue] looks at three-dimensional (3-D) trajectories of air arriving at Neumayer station for a 3 year

period, and at other destinations along the coast of the Weddell Sea for shorter periods. Although this information was not available for Dumont d'Urville, and not continuously for Halley, it will allow an assessment of the extent to which such techniques can contribute to understanding the origin of the chemicals found in air and ultimately in ice cores, and shows the kind of studies that will be necessary in the future.

Because all three sites are very close to some open water, sea salt is a dominant component by mass in aerosol at some periods. The paper on this topic [Wagenbach et al., this issue (a)] concludes that, except at the island station of Dumont d'Urville, the amount of open water is not the main factor determining the sea-salt concentrations in coastal Antarctica. The most critical finding is of the strong chemical fractionation of airborne sea-salt particles relative to seawater that evidently occurs at all three sites, and which leads (with the conventional calculation) to many negative values of non-sea-salt sulphate. The causes of the fractionation are evaluated, and a suggestion is made of a procedure for calculating a refined or corrected value of non-sea-salt sulphate, required for a meaningful discussion of the sulfur cycle in winter in particular. The cause of the fractionation appears to be precipitation of sodium sulfate, and this may occur on the surface of sea ice, suggesting that the mobilization of brine from the sea ice surface may dominate the winter sea-salt loading of the coastal Antarctic atmosphere.

All three stations experience rather high summer concentrations of both MSA and non-sea-salt sulphate. One paper [Minikin et al., this issue] discusses the seasonal cycle and compares its strength and seasonality at the three locations. These species are assumed to be derived from marine biogenic activity. An attempt is made to quantify the inputs of biogenic and nonbiogenic sulfur, and to estimate the latitudes from which biogenic sulfur originates in different seasons. A second paper [Legrand and Pasteur, this issue] looks more specifically at the MSA/non-sea-salt sulphate ratio. Next to sulphate, MSA is the second most important oxidation product of dimethylsulfide (DMS) emissions from marine biota, but in contrast to sulphate, DMS oxidation is the only source of MSA. MSA is therefore potentially an important tracer for biogenic sulphate production, and in particular the MSA/non-sea-salt sulphate ratio was suggested to be useful in distinguishing biogenic from nonbiogenic sulphate. This paper shows the complexity of factors influencing the ratio and discusses the combinations of temperature, oxidants, and transport that determine its value.

Nitrate in Antarctica is an enigma [Legrand and Kirchner, 1990; Wolff, 1995], with its sources still exceedingly uncertain. This species has been measured extensively in ice cores, and its use as a proxy for a host of different parameters (e.g., lightning frequency, solar activity, stratospheric temperature) has been suggested. However, no sensible use can be envisaged until its origin is better understood. A study of the nitrate seasonality at two of the sites [Wagenbach et al., this issue (b)] therefore offers a major opportunity to narrow down the possibilities. Using tracers for various sources, it is found that, although a tropospheric continental source may have some importance, nitrate brought from the stratosphere by PSCs probably plays a major role. Nitrate reemission from surface snow layers may also play a role within the inversion layer. One particular feature of the nitrate ice core record is that fresh snow concentrations are always higher than ice core concentrations. This suggests that loss of nitrate after deposition may also be important in interpreting the ice core record in terms of atmospheric concentration. The daily collection of surface snow at Halley allows a consideration of the importance and timescale of any such process [Mulvaney et al., this issue]. It appears that both losses and uptake can occur and that equilibrium processes are at work modifying initial nitrate concentrations.

At Dumont d'Urville, where a penguin colony is present very

near to the station, high concentrations of ammonium, oxalate, and of potassium and other cations are present. One paper [*Legrand et al.*, this issue] evaluates the effect, locally and on a continental scale of these penguin emissions. It also considers the far lower concentrations found elsewhere in Antarctica to evaluate the background oceanic emission of ammonium.

Much of the impetus for learning about the aerosol content of coastal Antarctica came from the desire to improve ice core interpretation. To this end, aerosol, fresh snow, and ice core data, particularly at Halley, have been compared throughout the year [*Wolff et al.*, this issue]. These data indicate the difficulty of obtaining a good relationship between air and snow chemistry on an event basis, although the seasonal patterns are clearly related. Wet deposition appears to dominate except for the largest particles, but blowing snow episodes confuse the picture.

The final paper concerns black carbon at Halley only [*Wolff and Cachier*, this issue]. These data are influenced first by contamination from the station itself, and they are used to assess the extent of that influence. After correction for this, the data are believed to reflect the residue of biomass burning at lower latitudes. Previously, for Antarctica, only a short record from South Pole has been available [*Hansen et al.*, 1988], so these data represent an opportunity to assess the long-range transport of this contaminant to the remote atmosphere of Antarctica. The paper shows that the seasonal pattern of black carbon in Antarctica is controlled by biomass burning, but strongly modulated by the efficiency of transport to Antarctica. The paper is able to confirm the negligible influence of black carbon on snow albedo and to consider what can be expected from ice core records of this parameter.

## 4. Conclusion

The sampling and analysis described in this paper have provided an opportunity to describe and interpret the aerosol chemistry of coastal Antarctica. This is important, not only because it represents a large unknown area, but also because of the large investment already made in ice cores from the Antarctic continent. A first step toward interpreting the data within the cores is to understand the natural variability of the atmosphere, and the coastal region is a good place to start, where manned stations, relatively high snowfall rates, and clear signals from the polar ocean, are available. The papers in this section provide some important insights into problems of atmospheric chemistry both within and outside the Antarctic region. The findings complement those obtained during summer only from the atmospheric sampling camp at Summit, Greenland, which are being used to aid interpretation of the Greenland Ice Core Project (GRIP) and Greenland Ice Sheet Project Two (GISP2) deep cores. The next challenge will be to obtain a similar knowledge for the Antarctic plateau, where the large ice coring projects of the next decade are currently taking place in an area whose atmospheric chemical properties are virtually unknown.

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