



Chemical Composition of Snow-Water and Scavenging Ratios over Costal Antarctica

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ABSTRACT

Snow samples and aerosol samples were collected at coastal Antarctica near Larsemann Hills and Maitri, during the 29th Indian Antarctic Expedition carried out during Dec., 2009 to March 2010. The main objective of this study was to characterize the chemical composition of fresh and surface snow at coastal Antarctica and to determine the scavenging ratios using composition of snow and aerosol samples. The pH of surface and fresh snow were 6.03 and 5.64 respectively. The surface snow samples were collected along a 127-km transect from the seaward edge of the ice shelf to the Antarctic plateau and analyzed for the presence of the major inorganic components SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , Na^+ , K^+ , Ca^{2+} and Mg^{2+} . It was observed that Na^+ and Cl^- were the most abundantly occurring ions at Antarctica. Considerable amount of SO_4^{2-} was also found in the both fresh and surface snow which may be attributed to the long range transport from Northern Hemisphere as well as to the oxidation of DMS produced by marine phytoplankton. A higher percentage of the ions in fresh snow may be because of trapping of the particulate matter in it. The sea-salt components i.e., Na^+ , Cl^- and Mg^{2+} decreased with increasing distance from the coast. The acidic components were neutralized mainly by NH_4^+ and Ca^{2+} . The scavenging ratio was maximum for Na^+ and minimum for NO_3^- , indicating that the scavenging efficiency was higher for coarse size particles and lower for fine size particles. In addition, we have attempted to find out the possible sources of the observed chemical species in snow-water.

Keywords: Antarctic snow samples; Chemical composition; Neutralization factor; Sea salt; Long-range transport.

INTRODUCTION

As one of Earth's most dynamically changing surface material, the structure of the snow changes in response to diurnal and seasonal changes in temperature. Snow is an important link between the atmospheric, terrestrial and oceanic systems. The snow pack can contain records that include climate change proxies, aerosol contaminant deposition rates and physical or photochemical alterations. As a consequence, research in the fields of snow chemistry and contaminants is aimed towards a better understanding of the scavenging and deposition of these types of contaminants on the snow pack and their subsequent post-deposition physical and chemical changes. Antarctica has a unique climate, which is the result of high altitude, perpetual snow cover, and great height of the ice plateau above the mean sea level and the vast extent of its surrounding ocean. The Antarctic weather is dominated by extreme cold and varies in both average and extreme temperatures. Hence, the

precipitation in the continent is mostly characterized by snowfall. Precipitating snow incorporates in it atmospheric aerosols and gases during nucleation. It coalesces with and collects the underlying aerosols during snowfall and traps them during deposition to the surface. Although dry deposition process provides a dominant sink mechanism on the Antarctic Plateau for the removal of atmospheric contaminants causing higher ionic contents in the snow pack than in precipitating snow (Gjessing, 1984), the scavenging process by snow predominates in the coastal Antarctica (Wolff *et al.*, 1998). The coastal Antarctica region is more affected by changing sea-ice extent and cyclonic activity than the high-altitude areas (King and Turner, 1997).

Antarctica provides the cleanest atmospheric environment available for study of the chemicals stored in snow and accumulated on the polar ice sheet, although the atmosphere of the Polar Regions is already affected by human activities (Legrand and Mayewski, 1997). In the last few decades, there has been a considerable increase in N-Hemisphere, anthropogenic activities both in developed and developing nations, which is responsible for an overall increase in the aerosol burden around the globe. Snow studies over sites such as Antarctica will help in estimating the background-level snow and aerosol, which could be compared with

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results obtained over polluted regions. Also, such a study helps in establishing a database that could be used in future for studying the long term impact of continuous human activities in increasing the background-level aerosol concentration. A number of studies regarding snow chemistry over various regions of the continent of Antarctica have been reported (Gjessing 1984; Sternberg *et al.*, 1998; Siegert *et al.*, 2001; Bertler *et al.*, 2004; Eija *et al.*, 2005; Beine *et al.*, 2006), but this kind of study over the region considered in the present study are meager. Ali *et al.* (2010) have presented concentration of only partial chemical constituents and pH value of a few samples of snow over a very limited region around the Maitri station. The present field study made at the Indian Antarctic Stations, LH and Maitri during the 29th IAE provides the observations at the stations in continuity to snow measurements made over Antarctica to understand the snow chemistry. The objectives of this paper are 1) to collect snow samples (fresh and surface) over the costal Antarctica to study their chemical composition, 2) to determine the scavenging ratios in remote costal environment using snow and aerosol samples (PM₁₀), 3) to characterize the possible sources of the observed chemical species in snow samples.

LOCATIONS OF SAMPLE COLLECTION, MEASUREMENT AND ANALYSIS

The LH (69°24'–69°25'S; 76°10'–76°3'E) is a relatively ice-free area, located approximately midway between the eastern extremity of the Amery Ice Shelf and the southern boundary of the Vestfold Hills on the Ingrid Christensen Coast, East Antarctica (Fig. 1). The LH area is marked by persistent, strong katabatic winds that gust from east to southeast during austral summer. The relative humidity is about 57% yearly basis. Daytime air temperatures from December to February at times exceed 4°C, with the mean monthly temperature a little above 0°C. Extreme minimum temperature recorded in the region so far is –40°C (Turner and Pendlebury, 2004). Pack ice is extensive in north-eastern side throughout the summer and the fjords and embayment

are rarely ice-free. Snow cover is generally thicker and more persistent on Stornes Peninsula than on Broknes Peninsula. Humans started arriving in this area since last 20 years, with the establishment of four scientific bases by Australia (Law Base), Russia (Progress I and II) and China (Zhongshan) situated around 10 km away in NE direction from the present observational site. All these stations are situated within a radius of 2.5 km from each other. Occasional ship-based tourist visits have also been made to the area since 1992.

The Indian station, Maitri (70°45'59"S; 11°43'50"E) is located in the Schirmacher oasis in the Dronning Maud Land, East Antarctica. The east-west trending Schirmacher oasis is exposed over an area of approximately 35 km² with 16 km length and a maximum width of 2.7 km in the central part (Fig. 1). Maitri is located ~80 km south of the coastal line. The area is dominantly covered by sandy and loamy sand type of soil. More details about station can be found in Ali *et al.* (2010). The sampling locations are shown in Fig. 1 and details are given in Table 1. The distance between LH and Maitri stations is around 2,300 km. For the collection of snow samples, clean hand gloves were used to minimize manual contamination. Snow samples were taken from untouched ground by means of a cutting frame with a surface area of approximately 0.3 m². We got chance to collect fresh snow (snow fall) samples at LH by using glass funnel of diameter 22 cm and glass bottle of 2000 mL (glass made of borosilicate). The amount of each sample collected was determined by weighing on an electronic balance. To prevent biological degradation in the snow water samples during storage and transport, a preservative (Thymol) was added in advance at IITM to the empty transport bottles. By this procedure any leakage/fall of Thymol in the station environment was eliminated. They were immediately put into plastic Ziploc bags, and then allowed to melt at the room temperature 25°C in the glass-ware. The snow melt water samples were subsequently passed through a Millipore filter for further analyses of pH & ionic content. After measuring pH and Conductivity samples were kept in cold storage (–20°C) for further lab analysis.

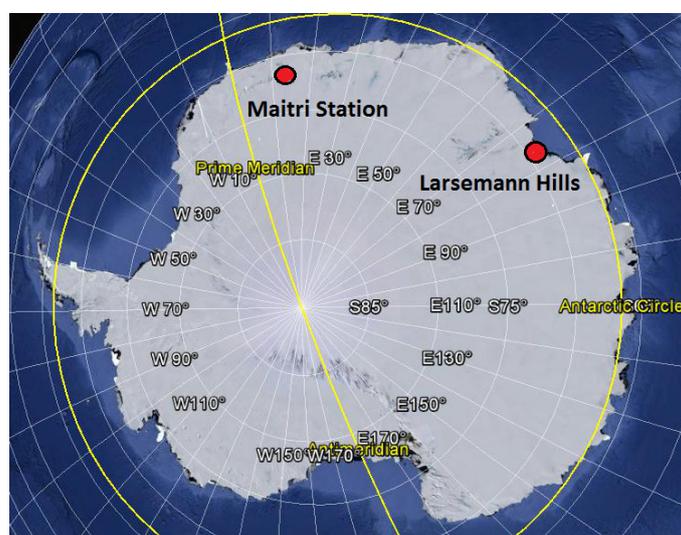


Fig. 1. Sampling locations of Indian research stations in Antarctica.

Table 1. Coordinates of sampling sites and distance from the ice edge.

Type of Sample	Sample ID	Date	Latitude	Longitude	Distance from edge (km)
Fresh snow (LH), N = 3	F1	27.12.2009	69°24'23"	76°12'40"	-
	F2	28.12.2009	69°24'23"	76°12'40"	-
	F3	29.12.2009	69°24'23"	76°12'40"	-
Surface snow (LH), N = 5	LS1	8.01.2009	70°03'3.4"	75°44'18.4"	27
	LS2	8.01.2009	70°03'13.4"	75°44'18.42"	68
	LS3	8.01.2009	69°33'58"	76°19'29"	26
	LS4	8.01.2009	70°09'44.2"	77°35'27.2"	107
	LS5	8.01.2009	70°25'12.5"	75°12'52.7"	121
Surface snow (Maitri), N = 7	MS1	19.02.2010	70°46'16"	11°39'00"	121
	MS2	19.02.2010	70°48'17"	11°43'12"	125
	MS3	19.02.2010	70°48'41"	11°39'41"	126
	MS4	19.02.2010	70°46'14.5"	11°36'14.3"	120
	MS5	19.02.2010	70°47'19"	11°40'50"	123
	MS6	19.02.2010	70°48'56"	11°39'41"	127
	MS7	19.02.2010	70°47'42.3"	11°36'14.3"	124

Aerosol (PM₁₀) samples were collected during 12 December 2009 to 4 February 2010 at LH using an air sampler (Envirotech Pvt. Ltd., India). Six samples at about 48 hours sampling period for each sample, were collected. Fliter papers used for PM₁₀ were Whatman (GF/A) Glass microfiber filter. Metler balance (Model AE 163) was used for weighing filters before and after exposure. The conditioned and weighed PM₁₀ filters were placed in cassettes and then in a cloth-lined envelope and taken to the field for sampling to avoid contamination of the filter papers on the way. For shipping, samples were encased in sealed plastic bag to minimize contamination. All blanks were shipped, stored and processed in an identical manner as the samples. The weighed filter papers were preserved in freezer until the completion of their extraction. PM₁₀ filter samples were extracted using a standard Soxhlet extractor for water soluble ions by using demonized water.

In the present study, we focus on the major ions of snow samples i.e. Na⁺, Mg²⁺, Ca²⁺, K⁺, Cl⁻, NO₃⁻, SO₄²⁻ and NH₄⁺. After the measurement of pH and conductivity, the melt waters were transferred to polyethylene bottles of 250 ml capacity rinsed thrice with deionized water. The pH and conductivities of the samples were measured immediately after the collection of the samples with the help of portable digital pH and conductivity meters. pH was measured with a digital pH meter, standardized at pH 4.0 and 9.2. Conductivity was measured with a digital conductivity meter calibrated against a reference KCl solution. Both pH and conductivity measurements were taken usually within 24 hours of collection. Concentrations of anions i.e., Cl⁻, SO₄²⁻ and NO₃⁻, were measured using Ion Chromatograph (DIONEX DX-100). Atomic Absorption Spectrophotometer (AAAnalyst 400) was used to measure cations i.e. Na⁺, K⁺, Ca²⁺ and Mg²⁺. The NH₄⁺ ion was measured by Indo-phenol Blue method (Weatherburn, 1967). HCO₃⁻ was calculated from pH using the relation, HCO₃⁻ = 10^{pH-5.05} (Safai et al., 2004).

QUALITY ASSURANCE

All analyses were performed in duplicate on different

aliquots of each sample. The error in analytical reproducibility for the major elements ranges from 0 to 5%. The Ion balance technique is widely used to check the quality of the data. Under this check, ratio between the sum of cations to the sum of anions both in µeq/L was estimated. The average ratio of sum of cations to the sum of anions for surface snow is 1.06 ± 0.06 and for fresh snow it is 1.05 ± 0.03 which are within the statistical limit, which indicates the good ionic balance. Another technique used for the snow-water data quality check was the comparison between measured and theoretically computed conductivities. Electrical conductivity (k, expressed as µS/cm) measurements of melted samples reflect the conductivity of all ions present in the sample (Hammer, 1983). Conductivity shows the ability of an aqueous solution to carry an electrical current and is used especially for melt-water quality control. Dissolved salts in solution carry the current and the conductivity is also dependent on the temperature. It is also partly influenced by the pH and the amount of atmospheric carbon dioxide, which has been dissolved in the water to form ions. The conductivity of snow cover is dependent on the season (Schlosser, 1999). The average difference between measured and theoretically computed conductivity for surface snow is 0.27 ± 0.34 and for fresh snow, it is 0.46 ± 0.09. Also, IITM has been participating in the international inter-comparison studies i.e., EANET's Inter-laboratory comparison projects and WMO's Laboratory Inter-comparison studies (LIS). The results from these comparison studies showed good agreement i.e., the variation is about ± 10%.

RESULTS AND DISCUSSION

As seen from Fig. 2 fresh snow at LH contain major ionic concentrations of Cl⁻ (32%), Na⁺ (30%) and Mg²⁺ (9%) together contributing (71%) to the total ionic composition, which indicates the dominance of sea source mainly due to the fact that the sampling location situated near the coastal area which is shown in Fig. 1. The main mechanism for sea-salt production over the open ocean is believed to be the bursting of air bubbles during whitecap formations and

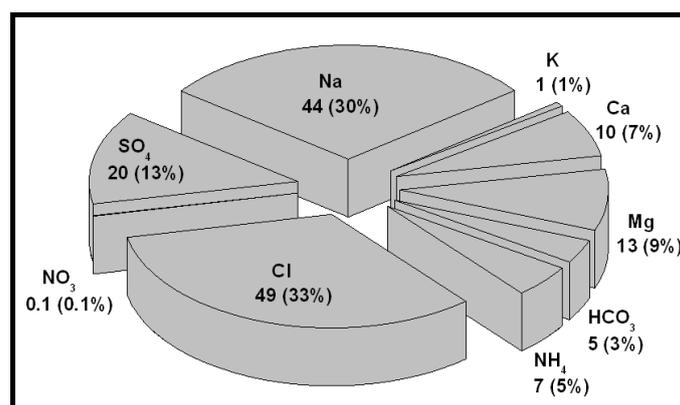


Fig. 2. Chemical composition of fresh snow water at LH in $\mu\text{eq/L}$ (Percentage contributions from different chemical is indicated in %).

dispersion of waves crests by surface winds (Blanchard 1983; Monahan *et al.*, 1986; Mulvaney *et al.*, 1993; Leifer *et al.*, 2000; Martensson *et al.*, 2003; Jaegle, *et al.*, 2010). Next to Sea-salt, SO_4^{2-} (13%) was found to be in high concentration that may be due to the long-range transport or due to the oxidation of DMS generated by marine phytoplankton as there is no major anthropogenic source at the sampling site and due to the remoteness of the site, human activities are limited. Some previous studies conducted over Antarctica showed that the oceanic dimethyl sulphide (DMS) can be a source of sulphur dioxide in Antarctica, also the ocean can be a source of primary and secondary organics (Gershey, 1983; O'Dowd *et al.*, 2004; Karkas *et al.*, 2005; Spracklen *et al.*, 2008; Asmi *et al.*, 2010). One more possible source is the Mount Erebus volcano located in coastal Antarctica (Ross Island, 3794 m above sea level) which continuously emits on an average 0.025 Mt of SO_2 per year (Andres and Kasgnosc, 1998). The contribution of Ca^{2+} was found to be very less i.e., 7%, which could be from surrounding mountain dust over the sampling site.

Spatial variations in ionic concentrations at LH site were large as seen from Table 2. The sea-salt ions showed the maximum spatial variation which decreased from the ice edge to the polar plateau. This indicates that the influence of sea salt aerosols on surface snow reduces with an increase in distance from the coast. Whereas, the other ionic components have not shown any trend with distance from the ice edge indicating their sources are other than marine.

Comparison between chemical composition of fresh and surface snow-water at LH are shown in Fig. 3. Except HCO_3^- , NO_3^- and K^+ concentrations of all the ionic species in fresh snow were higher (1.5 to 4 times) than those in surface snow. Where as, almost equal concentrations was observed for K^+ in fresh and surface snow samples. HCO_3^- and NO_3^- were less in fresh snow than in surface snow. The higher ionic concentrations in fresh snow than in surface snow may be due to the more local activity at the sampling site for fresh snow sampling. The surface snow samples were collected away from the local activities. The higher nss SO_4^{2-} nss Mg^{2+} and nss Ca^{2+} in fresh snow compared to that in surface snow indicates the influence of local activity.

Fig. 4 shows the comparison between ionic composition of

surface snow collected at Maitri and LH. The concentrations of all the ionic species were higher (by 1.5 to 9 times) at LH than the concentrations of corresponding ions in surface snow at Maitri. The increase at LH is minimum for Cl and maximum for NO_3^- . LH is situated on the hills of Prytz Bay. Along the coast, in summer time most peaks of the hills are open to soil. As research stations of china, Russia and India are situated in this area, the activities of Vessels, small boats and helicopters contribute higher ionic concentrations at LH than at Maitri.

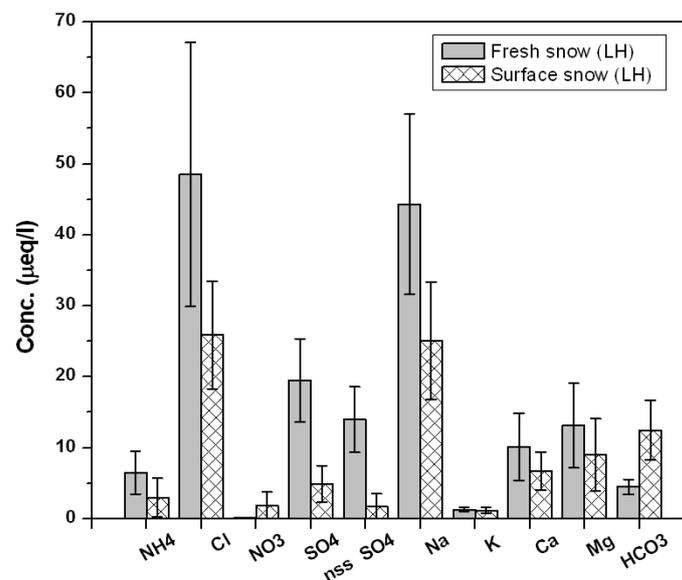
The pH and chemical composition of surface snow at Maitri in the present study is compared with that reported for the year 2004–05 at Maitri (Ali *et al.*, 2010) in Table 3. The average concentration of Ca^{2+} (2.7 $\mu\text{eq/L}$) in the present study is similar to the reported value of Ca^{2+} (2.5 $\mu\text{eq/L}$) by Ali *et al.* (2010). However, concentrations of the other ionic components were less in the present study compared to the earlier reported values. This may be due to the differences in the sampling locations as well as due to yearly variation of these components as is generally observed at other locations also. The SO_4^{2-} in the present study at Maitri (2.1 $\mu\text{eq/L}$) is nearly equal to that reported for James Ross Island (2.5 $\mu\text{eq/L}$) in the Antarctic Peninsula (Aristarain *et al.*, 2002).

The chemical components observed in the surface snow were attributed to a mixture of long-range transported substances from the southern Ocean and some local activities at these stations. The variation of ionic concentrations at these sites was very large and could have been due to wind redistribution, sublimation or post-depositional processes. This also reveals the importance of studies on spatial variation within single site to obtain good statistical estimates for the ionic concentrations and their variations. Previous glacio-chemical surveys showed the importance of careful data selection for Antarctica (Mulvaney and Wolff, 1994; Legrand and Mayewski, 1997; Kreutz and Mayewski, 1999). It is shown that snow chemistry concentrations vary by up to four orders of magnitude across Antarctica and exhibit distinct geographical patterns. However, the ionic concentrations in fresh and surface snow are very much less compared to the other geographical regions indicating that the Antarctic atmosphere is pristine.

Table 2. Mean concentrations of ions ($\mu\text{eq/L}$) in fresh and surface snow samples with standard deviations at LH.

Type of Sample	ID	n	pH	NH_4^+	Cl^-	SO_4^{2-}	NO_3^-
Fresh snow (LH)	F1	1	5.70	7.70	66.6	23.0	0.19
	F2	1	5.61	3.38	37.4	20.4	0.04
	F3	1	5.81	9.22	32.0	11.8	0.07
Surface Snow (LH)	LS1	4	6.09 ± 0.2	0.58 ± 0.2	35.1 ± 0.7	4.56 ± 0.3	4.86 ± 0.2
	LS2	3	6.26 ± 0.1	2.10 ± 0.1	29.4 ± 0.6	8.27 ± 0.4	1.68 ± 0.1
	LS3	3	6.18 ± 0.1	3.85 ± 0.1	27.5 ± 0.4	6.10 ± 0.4	0.50 ± 0.1
	LS4	3	6.15 ± 0.1	7.09 ± 0.2	19.6 ± 0.2	2.50 ± 0.3	0.16 ± 0.1
	LS5	3	5.74 ± 0.2	0.58 ± 0.2	16.3 ± 0.2	2.15 ± 0.3	0.02 ± 0.1

Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	nss SO_4^{2-}	nss Ca^{2+}	nss Mg^{2+}	M Cond
56.1	1.28	13.6	18.9	4.47	16.0	11.1	6.17	13.2
38.6	1.16	9.91	9.40	3.63	15.6	8.22	0.64	9.3
31.4	0.73	4.20	7.93	5.75	7.83	2.82	0.80	7.1
32.7 ± 0.6	0.75 ± 0.2	7.52 ± 0.4	14.0 ± 0.3	10.7	0.48	6.1	6.58	8.0 ± 0.1
31.3 ± 0.4	1.62 ± 0.2	8.51 ± 0.3	13.4 ± 0.2	16.2	4.36	7.1	6.29	7.2 ± 0.08
26.5 ± 0.4	1.41 ± 0.1	9.05 ± 0.3	6.58 ± 0.2	13.5	2.79	7.9	0.56	5.8 ± 0.02
18.0 ± 0.2	1.48 ± 0.2	4.09 ± 0.2	4.34 ± 0.1	12.6	0.46	3.5	0.25	4.2 ± 0.03
13.6 ± 0.2	0.93 ± 0.03	3.20 ± 0.2	3.17 ± 0.1	4.9	0.35	2.6	0.56	3.6 ± 0.05

**Fig. 3.** Comparison of fresh and surface snow at LH, Antarctica.

Source Identification

We have categorized snow-water ions into three main categories i.e., [a] Crustal (soil) [b] Marine and [c] Anthropogenic. Considering Na^+ as a reference for sea and Ca^{2+} for crustal, the non-sea salt (nss) and non-crustal [ncr] fractions for the measured chemical components of snow-water were calculated using standard crustal (Horn and Adams, 1966) and marine (Goldberg *et al.*, 1971) compositions. The fraction of the chemical component that remains after deducting sea salt and crustal fractions is considered as that from the anthropogenic sources.

Calculation of the Non-sea Salt Fractions

The non-sea-salt (nss) concentrations of K^+ , Mg^{2+} , Ca^{2+} , and SO_4^{2-} were calculated using Na^+ as the sea-salt tracer.

Nss SO_4^{2-} is computed as

$$\text{nss } \text{SO}_4^{2-} = [\text{SO}_4^{2-}] - \{([\text{SO}_4^{2-}]/[\text{Na}^+])_{\text{sea}} \times [\text{Na}^+]\} \quad (1)$$

where $([\text{SO}_4^{2-}]/[\text{Na}^+])_{\text{sea}}$ is the standard mass ratio of concentration of SO_4^{2-} and Na^+ which is obtained from sea water composition.

Similarly Nss fractions have been computed for the other chemical components. Sea salt (ss) fractions for these components were computed as

$$\text{Sea salt} = \{([\text{X}]/[\text{Na}^+])_{\text{sea}} \times [\text{Na}^+]\} \quad (2)$$

where, X is the desired component of snow for which sea salt fraction is to be calculated.

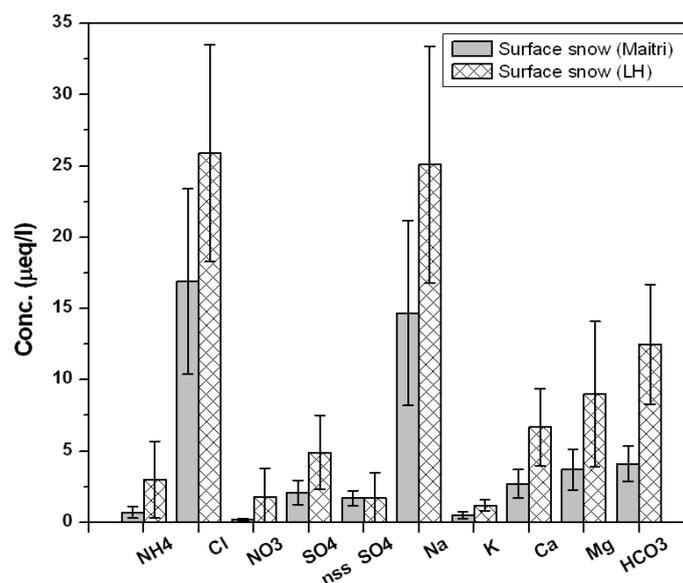


Fig. 4. Comparison of chemical composition of surface snow at LH and Maitri, Antarctica.

Table 3. Comparison of Surface snow chemistry at Maitri with the reported studies.

	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	NH ₄ ⁺	pH
Present Study	14.7	0.50	2.7	3.7	16.9	0.2	2.1	0.7	5.63
Ali <i>et al.</i> , 2010	49.4	2.7	2.5	15.0	55.6	0.6	31.2	5.6	6.1
Aristarain and Delmas, 2002	7.9	–	–	–	9.9	–	2.5		

After calculating the sea salt and non-sea salt fractions, the crustal fraction for different chemical components were computed by using nss Ca²⁺ as a reference element for crustal source.

For example, Ncr SO₄²⁻ is computed as:

$$Ncr\ SO_4^{2-} = [nssSO_4^{2-}] - \left\{ \left(\frac{[SO_4^{2-}]}{[Ca^{2+}]} \right)_{crust} X[Ca^{2+}] \right\} \quad (3)$$

where $\left(\frac{[SO_4^{2-}]}{[Ca^{2+}]} \right)_{crust}$ is the standard ratio of concentration of SO₄²⁻ and Ca²⁺ obtain from crustal composition. Also Ncr fractions have been computed for the other chemical components. Crustal (cr) fractions for these components were computed as

$$cr = \left\{ \left(\frac{[X]}{[Ca^{2+}]} \right)_{crust} X[Ca^{2+}] \right\} \quad (4)$$

It was observed that the crustal fractions of K⁺, Mg²⁺, SO₄²⁻ and Cl⁻ were in measurable amount. Crustal source was maximum in fresh snow (15.1%) and low at Maitri surface snow (6.1%) where the surface is mostly covered by snow and sampling locations are far away from coastline.

Marine or Sea Salt Sources

It was observed that in both fresh and surface snow-water samples the major contribution was from marine source and minimum from anthropogenic sources as shown

in Fig. 5. Among the three sets marine contribution was higher in surface snow at Maitri (92.7%) and lower in fresh snow at LH (74.4%). Sea salt particles are formed due to the wind action over the open ocean surface and sea ice. In atmospheric chemistry studies, either Na⁺ or Cl⁻ is generally chosen as the marine reference element, but magnesium Mg²⁺ has also been used (Legrand and Delmas, 1988). HCl was proposed as the major source for excess Cl⁻ in Antarctica, which is formed by the reaction of excess sulphate with sea-salt particles in the aerosol phase. The reaction is more efficient when weather conditions are calm, usually during summer. More than 90% of anthropogenic HCl emissions are confined to the Northern Hemisphere and only a tiny fraction of the emitted amounts of HCl is probably able to reach high southern latitudes (Legrand and Delmas, 1988). Ca²⁺ and K⁺ have two sources, a marine source as well as continental dust (Angelis *et al.*, 1992, Legrand and Mayewski, 1997). Ca²⁺ in precipitation is derived from soil dust (primarily as CaCO₃), while other Ca²⁺ sources in Antarctica include the marine aerosols (Gjessing, 1984). The crustal source appears to be less important to K⁺ than Ca²⁺ (Proposito *et al.*, 2002).

Enrichment factors (EF) are usually used for identify the origin of an element in precipitation (Zhang *et al.*, 2006). This calculation is based on the elemental ratio found between ions collected in the atmosphere or in precipitation, as compared to a similar ratio for a reference material. The EF values may imply for information about the source of the element. We used Na⁺ as a sea-spray indicator, assuming that sea spray is the only source of Na⁺ and that there is an

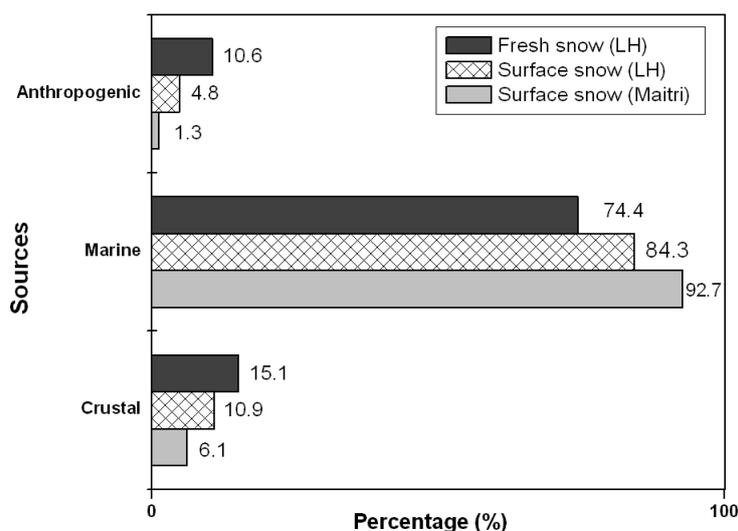


Fig. 5. Percentage contributions from different sources to the chemical ions in snow.

absence of selective fractionation processes and post-depositional effects. The enrichment factor, $EF(X)$, of element X was calculated from ionic concentrations in $\mu\text{eq/L}$ using

$$EF(X) = \frac{([X]/[Na^+])_{\text{Snow}}}{([X]/[Na^+])_{\text{Sea water}}} \quad (5)$$

When $EF > 1$, sources other than sea spray are present, When $EF < 1$, some fractionation has occurred. The EF for different ions for fresh and surface snow was shown in Table 4. EF were found to be high for Ca^{2+} for both fresh and surface snow samples; for SO_4^{2-} EF was high for fresh snow and for K^+ EF was high for surface snow at LH indicated other than sea sources, i.e., soil and long range transport, as there are no human activities especially biomass/fossil-fuel burning over this remote icy continent, the observed concentrations of SO_4^{2-} are most possibly from Northern Hemisphere. One more possible source is the Mount Erebus volcano located in coastal Antarctica. It is possible that the wind could have distributed small soil particles; originate from the open soil surfaces located nearby sampling sites, on the glacier surface, resulting in the elevated (Ca^{2+} and K^+) values. For the elevated $EF(SO_4^{2-})$ values, the DMS produced from the marine areas could also have oxidized to SO_2 in the atmosphere and the SO_2 may have further oxidized to SO_4^{2-} . During the air mass transport from inland regions, $nssSO_4^{2-}$ may have formed in aerosol particles due to conversion of SO_2 to SO_4^{2-} . The $EF(Cl^-)$ value remained near 1 indicates no enrichment. The nss calculations indicated that practically all of the Mg^{2+} originates from sea spray.

Various natural sources contribute to the sulphate (SO_4^{2-}) burden of the atmosphere, in addition to anthropogenic SO_2 emissions (Legrand and Pasteur, 1998). Dimethyl sulphide (DMS, CH_3SCH_3) emissions from the marine biota represent a major natural source of non sea-salt sulphate ($nssSO_4^{2-}$) in the remote marine atmosphere. In contrast to SO_4^{2-} the only atmospheric source for methane sulphonic acid (MSA, $CH_3SO_3^-$) is the oxidation of DMS (Legrand and Pasteur, 1998). The MSA to $nssSO_4^{2-}$ ratio has been used in

evaluating the contribution of biogenic sources to total SO_4^{2-} over the area and typically shows a summer maximum and a winter minimum. Colder temperatures favour the formation of MSA and could have played a crucial role in controlling the final composition of the high southern latitude atmosphere over the last climatic cycle (Legrand *et al.*, 1992).

Anthropogenic Sources

The anthropogenic source comprised of sum total of the non sea salt and non crustal fractions of all the above mentioned chemical components except NO_3^- and NH_4^+ as these components don't have any crustal or marine contribution. Contribution of anthropogenic source was observed to be very low for surface snow at Maitri (1.3%) and comparatively more in fresh snow at LH (10.6%). Nitrate (NO_3^-) in polar snow is mainly due to the deposition of gaseous nitric acid (HNO_3), an acid that is the end product of the oxidation of various nitrogenous trace gases (NO_x). Jones *et al.*, (2008) recorded the photochemical production of nitric oxide and nitrogen dioxide (NO and NO_2) in Antarctic snow cover. On the other hand NO_3^- has been found to be affected by post-depositional losses at locations of low accumulation (Röthlisberger *et al.*, 2000). Ammonium (NH_4^+) is mainly released from combustion, bacterial decomposition of plant matter in soils and bacterial decomposition of excreta. In the high southern latitudes the primary natural source of NH_4^+ is biogenic oceanic emissions (Legrand *et al.*, 1998) and, to a lesser extent also, animal waste. Thus, as the Antarctica location is relatively free from major urban pollution sources and mostly covered by snow, contribution from both anthropogenic and crustal sources was less compared to the marine source.

Neutralization Factor

Measurement of all major cations and anions in a sample make it possible to evaluate the effectiveness of the alkaline cations in neutralizing the acidity produced by the anions in the sample. The neutralization potential of an alkaline cation is judged by the magnitude of its neutralization

Table 4. Comparison of Sea water ratios with snow water with respect to Na⁺ and Enrichment Factors.

	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻
Seawater ratio	0.022	0.044	0.227	1.16	0.125
Fresh snow ratio (LH)	0.03	0.23	0.29	1.10	0.44
Surface snow ratio(LH)	0.05	0.27	0.36	1.03	0.19
Surface snow ratio (Maitri)	0.03	0.18	0.25	1.15	0.15
EF Fresh snow	1.36	5.21	1.31	0.94	3.53
EF surface snow (LH)	2.13	6.08	1.57	0.89	1.55
EF surface snow (Maitri)	1.47	4.13	1.10	0.99	1.16

factor (NF) which is given by the ratio of the concentration of nss fraction of the particular cation to the sum of the concentrations of the acid producing anions. Among the measured anions in the snow, NO₃⁻ and nss SO₄²⁻ are the major acid producing anions, whereas Ca²⁺, NH₄⁺, Mg²⁺ and K⁺ are the major acid neutralizing cations.

Neutralization Factor (Nf) of a particular cation is calculated as:

$$\text{Nf X} = \text{X}/[\text{NO}_3^- + \text{Nss SO}_4^{2-}] \quad (6)$$

where X = the cation for which Nf is calculated e.g., Ca²⁺, NH₄⁺, Mg²⁺ and K⁺. The percentage contribution of neutralization factor for major cations in snow-water at LH and Maitri are shown in Fig. 6. It was observed that the maximum neutralization in surface snow at Maitri was due to Ca²⁺, whereas at LH, in both fresh and surface snow, the maximum neutralization was due to NH₄⁺ followed by Ca²⁺.

Scavenging Ratios

The scavenging processes of material in the coastal atmosphere depends on the size distribution of the aerosol, the relative mix of the pollutants and sea salt, kinetics and the convective mixing of coastal air masses. The efficiency of scavenging processes over the ocean and coastal part of Antarctica can vary for chemical species. It occurs by both forms of deposition i.e. wet and dry processes. The wet processes include the nucleation of marine clouds primarily by aerosol. The dry processes include coalescence of aerosols which involves primarily Sea salt in the marine boundary layer.

The scavenging ratio is defined as the concentration of the species in rain, snow and fog (A) to its concentration in air (B). These ratios derived from air collected near the earth's surface and from precipitation formed at higher altitudes can be difficult to interpret (Patterson and Settle, 1987). These concentrations are usually expressed on a volume or mass basis; the volume or mass-basis scavenging ratios in the reported studies, which differ by a factor equal to the density of air (ρ) = 1.2 gm³.

$$\text{Scavenging ratio (W)} = \text{A/B X } \rho \quad (7)$$

Scavenging ratios are not the only means by which wet deposition is computed. Some researchers referred as scavenging rates, scavenging coefficients, and rainout efficiencies (Hidy and Countess 1984; Hicks, 2005). Scavenging ratios for various ionic components over the

coastal Antarctica were calculated and are shown in Table 5. Scavenging ratios also depend on the size of the aerosol. Marine scavenging ratios are observed to increase with an increase in size of the scavenged aerosol (Church *et al.*, 1990, Budhavant *et al.*, 2010). Maximum scavenging ratio was found to be for Na⁺ and minimum for NO₃⁻. This indicates that the scavenging efficiency was higher for coarse size particles like Na⁺, Mg²⁺, and Cl⁻ and lower for fine size particles like NO₃⁻ and NH₄⁺. Some portions of nitrate are likely to be associated with sea salt aerosols. Chemical interactions between nitric acid and sea salt in coastal regions results in rapid phase change in total NO₃⁻ (HNO₃⁻ + particulate NO₃⁻) from predominantly HNO₃⁻ to predominantly super- μm diameter aerosols. Lifetime of super- μm sea salt aerosols against deposition is different to that of gases nitric acid and fine mode ammonium. Therefore, nitrate is often found in coarse size range. The reason of low scavenging ratio for nitrate might be attributable to snow-air recycling of nitric acid (e.g., Jarvis *et al.*, 2009). This feature suggests that the scavenging ratio is directly proportional to the particle size. The dependence of scavenging ratio on particle size is also reported earlier (Jaffrezo and Colin 1988; Cadle *et al.* 1990; Budhavant *et al.*, 2010).

CONCLUSIONS

The chemical analysis of snow in the background areas of Antarctica in summer during Nov. 2009–March 2010 revealed the following.

1. Average pH value for fresh snow was 5.74 and that for surface snow was 6.04 indicating the fresh snow is neutral and surface snow is slightly alkaline.
2. The concentrations of all the ionic species in surface snow were higher (by 1.5 to 9 times) at LH than those at Maitri. As research stations of China, Russia and India are situated in this area, the activities of vessels, small boats and helicopters seem to have contributed to the higher ionic concentrations at LH than at Maitri.
3. The Na⁺ and Cl⁻ showed maximum concentrations among the cations and anions, respectively in both the fresh and surface snow samples indicating dominance of marine source.
4. Neutralization of acidic components in snow was mainly due to NH₄⁺ and Ca²⁺ followed by Mg²⁺.
5. The scavenging ratio was maximum for Na⁺ and minimum for NO₃⁻, indicating that the scavenging efficiency was higher for coarse size particles and lower for fine size particles.

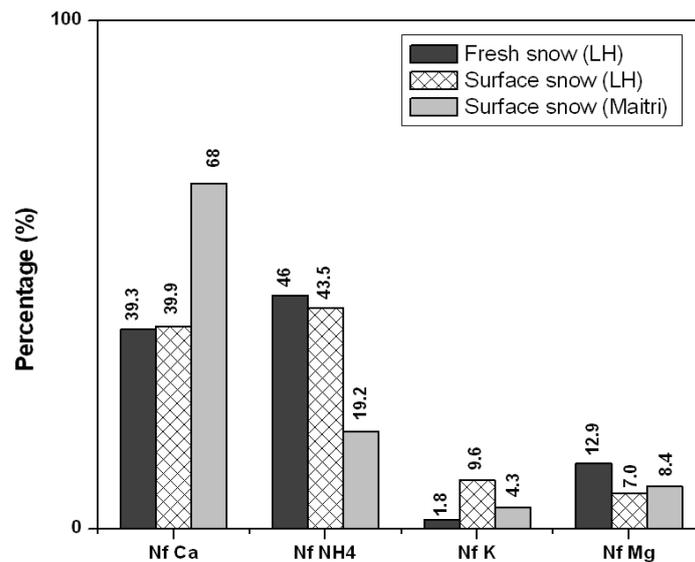


Fig. 6. Percentage contributions of Neutralization factors for different cations in snow water at LH and Maitri, Antarctica.

Table 5. Scavenging ratios of various ionic components over coastal Antarctica.

Ions	Conc. in Snow ($\mu\text{g/g}$) A	Conc. in Aerosol ($\mu\text{g/m}^3$) B	Scavenging ratio (W) A/B X ρ
Na^+	0.967	0.279	4158
Mg^{2+}	0.145	0.045	3882
Cl^-	1.609	0.538	3590
SO_4^{2-}	0.883	0.321	3302
Ca^{2+}	0.185	0.093	2376
K^+	0.041	0.021	2311
NH_4^+	0.122	0.142	1029
NO_3^-	0.006	0.030	247

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