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Studies on surface and sub-surface snow samples from the coastal and inland regions of East Antarctica (Program #9)

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ABSTRACT

A snow coring program was initiated in two geographically distinct regions across East Antarctica during the austral summer of 2008-2009 with primary focus on glaciochemical and stable isotope studies. The field work concluded with a successful completion of two major coastal to inland transects covering a total distance of 380 km and a maximum elevation of 3000 m a.s.l. These transects fall in two different sectors of East Antarctica - the central Dronning Maud Land facing the Atlantic sector and the Princess Elizabeth Land facing the Indian sector of the Southern Ocean. A total of 44 snow cores (~1m each) and surface snow samples were recovered following strict contamination-free sampling protocols. The snow core samples are being studied for chemistry and stable isotopes after sub-sampling at the -15°C processing facility in the ice core laboratory. The ionic components were measured using ion exchange chromatography in μgL^{-1} levels. Stable water isotopes (oxygen and hydrogen isotopes), trace elements, total organic carbon, and dust particle quantification were also carried out on these samples. A multi-proxy biogeochemical approach is being involved while interpreting the results from these snow cores and surface snow samples. Preliminary results from glaciochemical investigations of these snow samples are outlined in this report.

INTRODUCTION

The major constituents of the Antarctic snow and ice are the sea-salt ions (Na^+, Cl^-, SO_4^{2-}, K^+, Mg^{2+} and Ca^{2+}), the atmospheric acids (H_2SO_4 and HNO_3) along with minor amounts of biologically derived components (MSA and NH_4^+) and other organic acids (Hall and Wolff, 1998). Along with these components, natural mineral dust from local and long range transported sources are significant which bring in trace metals and anthropogenic pollutants to the Antarctic snow (Laluraj et al. 2014). It is also shown that Antarctic snow and ice act as a significant organic carbon reservoir (Priscu et al. 2008). Many snow studies in Antarctica are based on surface snow deposits (Kärkäs et al. 2005; Thamban et al. 2010; Antony et al. 2010), and spatial variability in Antarctica are mainly attributed to the site-

specific features like elevation, distance from the sea and, snow accumulation (Bertler et al. 2005). An improved understanding of the spatial and seasonal variability is necessary to understand various aspects of the air-snow transfer processes of the above mentioned components, which in turn are necessary to enhance the interpretation of signals from ice core records. However, in order to understand the seasonal and annual variations and the factors that influence various proxies, samples from pitting and shallow-coring representing multi-seasonal snow deposits are essential.

Objectives:

The following objectives were set for the shallow snow coring program during the XXVIII Indian Scientific Expedition to Antarctica.

- To quantify the spatial variations in the seasonal distribution of glaciochemistry, snow accumulation and trace elements from two distinct regions (Atlantic and Indian Ocean sectors, > 2000 km apart) in East Antarctica.
- To assess the air-snow-air transfer processes and biogeochemical cycling in Antarctic snow.

This study ensures the collection of snow cores of same age from two distinct regions, which helps in understanding the contrasts in spatial variation of biogeochemical cycling of various chemical species as well as of the factors affecting various proxies brought about by the changes in the surrounding ocean. The coupling of isotope and chemical profiles from two regions will help in understanding various atmospheric and oceanic processes influencing the seasonality of snow chemistry. This work will contribute to the data integration in the snow chemistry database initiated by the International Trans Antarctic Scientific Expedition (ITASE).

STUDY AREA

The study area is located in two different regions - central Dronning Maud Land (cDML) and the Princess Elizabeth Land (PEL), facing the Atlantic and Indian Oceans respectively. Both these regions are ~ > 2000 km apart even though they are within the East Antarctic ice sheet. Geographical and topographical differences are significant between these two regions. The cDML region is influenced by the presence of an ice shelf - Nivlisen ice shelf - thereby effectively increasing the distance of the ice sheet from the open ocean. On the interior, a chain of exposed mountains - Wohlthat mountains - influence the surrounding area to an extent by blocking the flow of katabatic winds from the interior of the continent.

MATERIALS AND METHODS

Sampling: Unlike the number of studies on the western Antarctic ice sheet, Princess Elizabeth Land and central Dronning Maud Land are among the least studied regions in terms of seasonal and spatial variations in snow chemistry. Previous studies in these regions indicate that the coastal area is dominated by a steep escarpment zone influenced by katabatic winds (Allison, 1998), while the maritime winds are constant at the coastal sections (Ma et al., 2010). In order to study the effect of rapid elevation changes and the interacting wind regimes on the chemistry of snow, adequate planning was made to sample along a transect perpendicular to the elevation contours prior to field sampling (Fig.1).

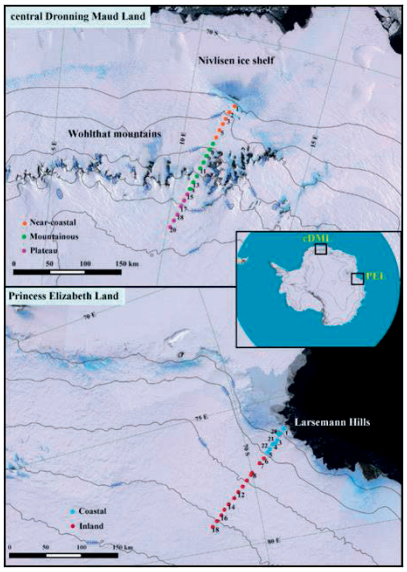

Fig.1: Transects showing sampling locations at cDML and PEL regions of East Antarctica. Inset showing the study regions in Antarctica.

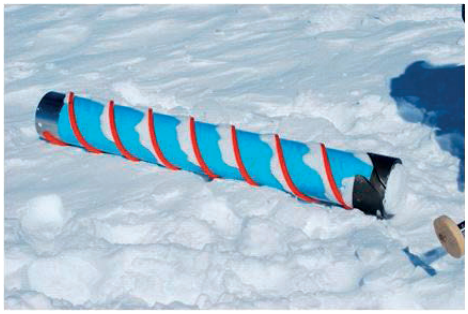

Fig.2: Snow coring with KOVACS Mark IV Coring system.

Snow core and surface snow samples were collected from the cDML and PEL transects. Helicopter support was utilized during sampling in order to successfully cover the coastal and inland regions of the transect. Snow cores were drilled using a KOVACS Mark IV coring system (14 cm diameter) (Fig.3) during this expedition. Sampling was carried out ~ 50 m upwind from the landing site of the helicopter in order to avoid contamination. Each snow core was about 1 m deep and covered more than 1 year of snow accumulation. A total of 21 snow cores and surface snow samples were retrieved from PEL covering a distance of 180 km from the coast and covering an elevation of 2100 m a.s.l. Similarly, in cDML, 20 snow cores and surface snow samples were retrieved from the near coast to the inland region, covering a distance of 110-300 km from the coast and an elevation of 2800 m a.s.l. As mentioned previously, the Nivlisen ice shelf increased the distance of the open ocean to sampling region by about 100 km and for the sake of clarity only the actual distance from the open ocean is mentioned in cDML transect. The surface snow samples and snow cores were transferred directly into pre-cleaned high-density polyethylene bags and sealed immediately to avoid any contamination during storage and transport. The sample bags were stored at -20°C throughout the transit to the ice core laboratory of National Centre for Antarctic and Ocean Research.

Fig.3: Sampling was carried out ~50 m upwind from the helicopter landing site.

Processing and Analyses: Sub-sampling of snow cores at 5 cm resolution was carried out under clean conditions in a laminar-flow bench, housed in the processing facility at a -15°C cold room. All sub-sampling equipment and sample containers were pre-cleaned by rinsing several times with Milli-Q water (18 M Ω), soaking for at least 24 hours, followed by rinsing with fresh Milli-Q water and drying in a laminar-flow bench. Samples were melted immediately prior to the analysis in a class 100 clean room

facility. Cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) were analyzed using a Dionex DX-2500 with IonPac CS17 column and anions (Cl^-, MSA^-, SO_4^{2-} and NO_{3-}) were analyzed on a Dionex ICS-2000 with IonPac AS11-HC column. The detection limits were within 2 $\mu gL^{-1}$for most of the ions except NO_3- and Cl^- which had a detection limit of 5 μgL^{-1}. Reference standards and random samples were analyzed routinely to estimate the analytical precision which was better than 5% for all the ions. For Cl^- and NH_4^+ the precision was within 10%. More details of ion chromatography methods are described elsewhere (Mahalinganathan et al. 2012, 2016). Dust particle concentration and grain size measurements were carried out using a Multisizer 4 Coulter Counter (Beckman), placed in a class 100 clean room. Size calibration was made using polystyrene latex beads of 5 µm radius and a precision better than 5% was obtained. The total organic carbon (TOC) measurements were made using a high-sensitivity TOC analyzer (Shimadzu TOC-VCPH) with a precision better than 5%. A detailed description of the TOC analyses is provided in Antony et al. (2011). The stable oxygen and hydrogen isotopes records were measured using a dual inlet, Isoprime Isotope Ratio Mass Spectrometer following standard analytical procedures (Naik et al., 2010). The external precision obtained using a laboratory standard (CDML 1) on oxygen and hydrogen isotope analyses was ±0.05‰. The seasonality of snow cores was determined using the $\delta\ ^{18}O$ records and sea-salt chemistry records (Mahalinganathan et al., 2012; Mahalinganathan and Thamban, 2016).

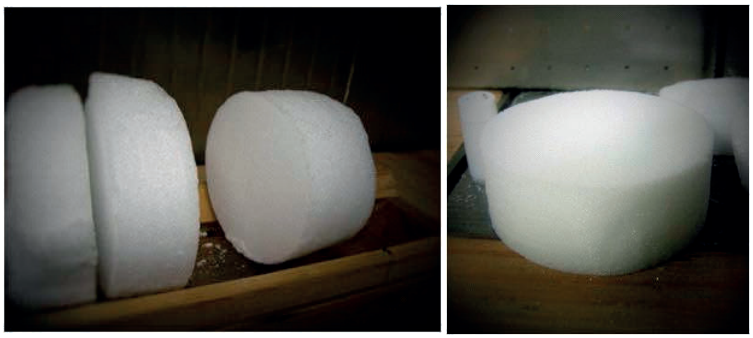

Fig.4:Core Processing: Snow cores were processed at 5 cm resolution at -15°C ice core lab facility at NCAOR. Snow pack density was measured during processing.

RESULTS AND DISCUSSION

Topography and snow chemistry variation

This study using annual snow core records from the coast to inland transect in Princess Elizabeth Land revealed significantly low Cl^-/Na^+ ra-

tios within 50 km from the coast (Fig. 3). These sites are also characterized by a steep slope that decreases significantly inland. Strong correlation between slope and Cl^-/Na^+ ratio suggests a predominant influence of slope on sea-salt chemistry of snow. Seasonal patterns revealed that Cl^- concentrations were significantly lower than that of Na^+ on the steep zones throughout the year. The maritime air masses and the katabatic winds strongly interact in the coastal Antarctic regions, with the steep coastal slopes aiding in preferential deposition of sea-salt aerosols in snow. The wind redistribution of snow, influenced by the slope variations increase the Na^+ concentration, thereby lowering the Cl^-/Na^+ ratios and a possible overestimation of sea-salt fractionation along the steep slopes. We propose that higher concentrations of Na^+ with Cl^- loss in snow are primarily driven by the steep slopes of coastal Antarctica. An elaborate discussion is published in a peer reviewed journal (Mahalinganathan et al. 2012).

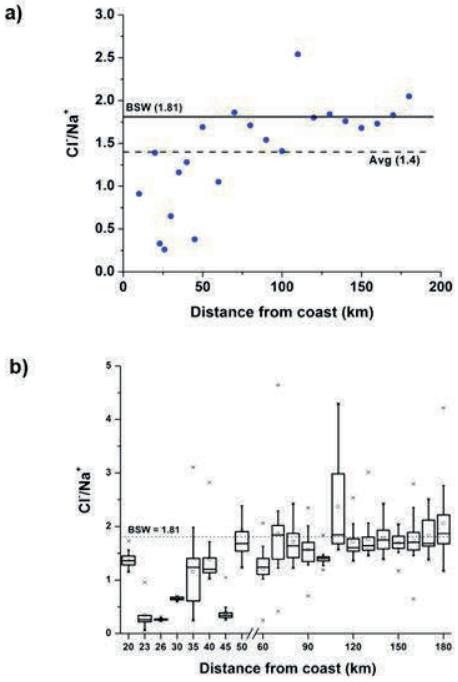

Fig.5: Average annual Cl/Na ratio from coast to inland. The dashed line is the ratio of Cl/Na in bulk sea water.

Sources of NO_3^- in Antarctic snow

A strong and widespread association between $nssCa^{2+}$ and NO_3^- in snow was observed from both PEL and cDML regions (Mahalinganathan

and Thamban, 2016). We hypothesize that such a strong association is due to the interaction between calcium-rich dust and nitric acid in the atmosphere, resulting in the formation of $Ca(NO_3)_2$ aerosol. The results from ionic balance and residual acidity show that a majority of NO_3^- in the coastal region is associated with $nssCa^{2+}$ (as $Ca(NO_3)_2$), whereas in the inland region NO_3^- was associated with H^+ (as HNO_3) (Fig.4). The forward- and back-trajectory analyses suggest that fine calcic mineral dust from the SSA region has been transported to the East Antarctic region, aided by the westerlies. Also, the results from principal component analyses strengthen our view that $Ca(NO_3)_2$ was formed in the atmosphere during the transport of the mineral dust from southern South America tothe East Antarctic region. Our study also shows that local input of dust and sea-spray is more likely to mask the association between calcium and nitrate. We propose that, apart from other significant NO_3^- sources, nitrate associated with mineral dust could form a significant portion of total NO_3^- deposited in the East Antarctic snow. An elaborate discussion is published in Mahalinganathan and Thamban, 2016.

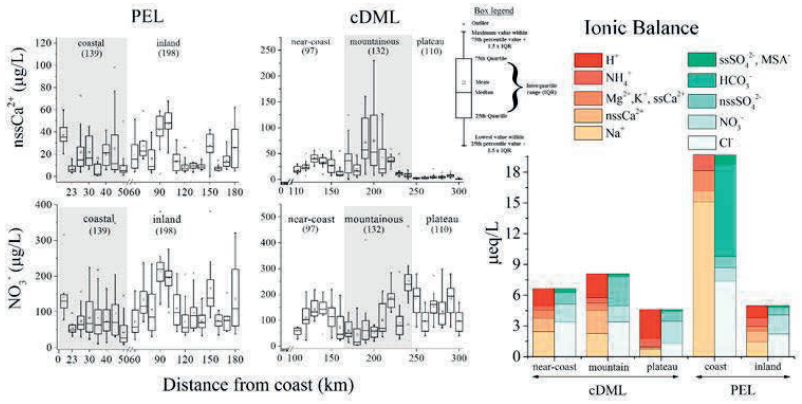

Fig.6:Plots showing the distribution of $nssCa^{2+}$ and NO_3^- in PEL and cDML transects. Ionic balance graphs show the contribution of each individual ions from all snow cores.

Organic carbon and dissolved organic matter: Sources and spatial trends

Organic carbon records of the surface snow samples from both PEL and cDML regions showed that TOC exhibited considerable spatial variation with significantly higher values in the coastal samples Antony et al. (2011). However, limited variations were observed in TOC concentrations beyond 100 km from the coast. Both distance from the sea and elevation influenced the TOC concentrations. The in situ microorganisms accounted

for 365 and 320 ng carbon L^{-1} in PEL and cDML, respectively. A detailed discussion is published in Antony et al. (2011). In addition, molecular level characterization of dissolved organic matter in snow was carried out using ultra-high resolution mass spectrometry. Tens of thousands of distinct molecular species were identified, providing clues to the nature and sources of organic carbon in Antarctica. The study demonstrated that many of the identified supraglacial organic matter formulae are consistent with material from microbial sources, and terrestrial inputs of vascular plant derived materials are likely more important sources of organic carbon to Antarctica than previously thought. Black carbon-like material apparently originating from biomass burning in South America is also present, while a smaller fraction originated from soil humics and appears to be photochemically or microbially modified. In addition to remote continental sources, signals of oceanic emissions of primary aerosols and secondary organic aerosol precursors have also been documented. Results suggest that a much more complex and reactive carbon pool is associated with supraglacial environments than previously thought. A detailed discussion is published in Antony et al. (2014).

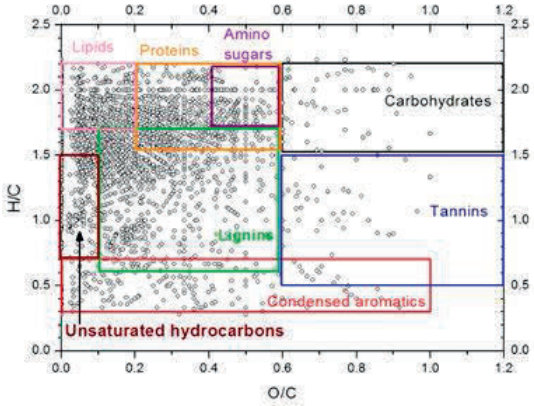

Fig.5: Major biochemical compound classes detected in surface snow samples. The colored boxes represent compositions for major compound classes. Overlapping boxes are distinguished by nitrogen content or aromaticity index.

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SCIENTIFIC OUTPUTS FROM PROGRAM#9

Peer reviewed publications

K MAHALINGANATHAN AND M THAMBAN.(2016). Potential genesis and implications of calcium nitrate in Antarctic snow. The Cryosphere, v.10(2), pp.825-836, doi: 10.5194/tc-10-825-2016. IF - 5.52

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PhD Theses associated with snow samples from program#9

RUNA ANTONY(2016). Bacteria and their role in organic carbon dynamics in Antarctic snow. Department of Marine Science, Goa University.

MAHALINGANATHAN K(2017). Chemical and stable isotope records of Antarctic snow and its implications on palaeoclimate studies, Department of Earth Science, Goa University.

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