

Trace elemental variability in aerosols near the two Indian Antarctic research stations during austral summer

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ABSTRACT

Sampling of aerosols was carried out at two East Antarctic sites during 20th January to 3rd February 2009 at Larsemann Hills (LH) and 23rd February - 7th March 2009 near Maitri station at Schirmarcher Oasis (SO), using a high volume sampler. The elemental concentration was analyzed through Ion Chromatography. Sea salt aerosol (Na) dominated the elements forming 90-92% of the total elemental mass concentration. Crustal aerosols were enriched with Sc and Co whereas Mo, Cd, Sb enrichment in aerosols indicated anthropogenic sources in both the study regions. Further, the Efc of Pb showed crustal source in Larsemann Hills but anthropogenic influence in aerosols near Maitri at Schirmarcher Oasis. During blizzards, the aerosols were found to be enriched with anthropogenic elements like Cd, Mo and Cu at both the sampling sites. This enrichment of aerosols with trace elements during blizzard events could be of important implications since one event can deposit 2-3 fold higher concentrations of trace elements on the snow, as blizzards are often accompanied by snow fall and snow drift. Further the rocky outcrops of Larsemann hills play a significant role in generating coarse crustal aerosols enriched with Co, Cr and Pb and the station activities near Maitri enrich the aerosols with Sb and Pb. This study not only draws a comparative analysis of aerosols at two east Antarctic sites but also provides the baseline data on aerosol trace elemental concentration before the third Indian Antarctic station, Bharati was commissioned at Larsemann hills.

Keywords: crustal aerosols, anthropogenic, enrichment factors, East Antarctica

1. INTRODUCTION

Antarctica provides the cleanest atmospheric environment, relatively untouched by human activities and isolated by the southern ocean an circumpolar vortex from neighbouring continents. This provides an ideal opportunity for studying the background of aerosols far from other continents (Artaxo et al., 1992, Mouri et al. 1997, Arimoto et al. 2008). These high latitudes are experiencing more rapid climate change than other regions in our planet which makes them an important natural laboratory to observe the changing climatic effects and further initiate effective environ-

ment management plans for their preservation. To decipher the anthropogenic inputs related to the increasing research station activities in Antarctica, it is essential to have a baseline data on the trace metal composition of the aerosols and their possible sources. Various particulate and aerosol material are atmospherically transported over Antarctica (Lambert et al., 1990) and get deposited on the snow. However, the mechanisms involved in aerosol transport and possible sources are not fully understood (Ikegawa et al., 1997). Although some studies have documented the human impact on the Antarctic environment (Wolff et al., 1999; Tin et al., 2009), the definition of natural baseline levels of trace metals in Antarctic snow and their spatial and temporal variability are still largely unknown. Considering the role of Antarctica as a gauge of global contamination levels and trends, such studies have significant scientific rationale (Gasparon & Matschullat 2006). In order to better understand the human interferences in the heavy metal cycling in Antarctic atmosphere and thus impacting the snow deposits, spatially distributed studies are crucial. The study of trace metals in Antarctica has been carried out since 1974 to study the long range impact of continental pollution (Maenhaut et al., 1983; Weisel et al., 1984, Arimoto et al., 1985, Arimoto et al., 1987 Zhou et al., 1990). Such studies revealed that large-scale pollution of elements like Pb started in the most remote areas of Southern Hemisphere since the 1880s and for elements such as Cr, Cu, Ag, Bi, and U since the beginning of the twentieth century. Previous observations of trace elements in aerosols were made at South Pole (Duce et al., 1975, Zoller et al., 1974; Arimoto et al., 2008) coastal West Antarctica (Mishra et al., 2004; Saxena & Ruggiero 2013) and coastal east Antarctica (Xu & Gao 2014). Since seasonal patterns of heavy metal concentrations deposited in snow have been observed in Lambert Glacier basin, East Antarctica (Hur et al., 2007) and signatures of human inferences on east Antarctic snow have also been documented (Thamban & Thakur 2013), atmospheric trace elements over coastal East Antarctica (CEA) need to be studied to infer the sources, mechanisms of transport and deposition of trace elements to Antarctic snow.

The source of heavy metals in Antarctic snow is predominantly the dry or wet deposition of crustal and anthropogenic aerosols (Lambert et al., 1990) and these mechanisms depend on the meteorological conditions and geographical setting of the Antarctic stations, whether coastal or inland. The ionic chemistry of Antarctic aerosols has been studied both at the coastal stations like, Syowa Station, Neumayer Station, Halley Station, Dumont d'Urville Station, and Mawson Station (Savoie et al., 1993; Legrand et al., 2001; Hara et al., 2004; Weller et al., 2011) as well as inland stations as Amundsen-Scott (South Pole) Station, Dome F Station, Kohnen Station,

and Concordia (Dome C) Station (Weller and Wagenbach, 2007; Jourdain et al., 2008, Eisele et al., 2008, Udisti et al., 2012). These studies show variable ionic composition, seasonally as well as spatially. These studies need to be complemented with the trace elemental composition of aerosols which is relatively sparse in these Antarctic stations. Hence, to add to the existing knowledge on the trace elemental composition of aerosols this study was undertaken at the two Indian Antarctic station sites, Schirmacher oasis (SO) and Larsemann hills (LH). This study at Larsemann hills provides the baseline data on aerosol chemistry before the third Indian Antarctic station, Bharati was commissioned here.

Study Area

Aerosol sampling was carried out at two sampling stations in East Antarctica, Maitri located at Schirmacher oasis (SO) and Larsemann Hills (LH). The two locations have distinct geographical features. Maitri, the 2nd permanent Indian Antarctic research station is situated on a rocky area, 500m from the continental ice which is 75 km away from the open ocean (Fig 1). The Russian Novo station and an airbase are situated 7km towards the east and 12km south west respectively to Maitri. The station activities are supported by the electrical generators and have a capacity to house 75 persons during summer and 25 in winter. In contrast to Maitri, the sampling location on LH Island was relatively more pristine since at the time of sampling in 2009 India's third Antarctic station was not built. LH is an ice-free oasis on the Ingrid Christenson Coast and extends as a coastal outcrop on the eastern side of Prydz bay (Fig.1). It represents a significant portion of the ice-free area of the East Antarctic coastline (Thamban et al., 2010). During the sampling in Jan- Feb 2009, the Third permanent Indian station was not established. Therefore the aerosols samples collected during this time period can be considered for baseline comparison for further studies after the commissioning of Bharati station in 2012. The aerosol sampling was carried out through high volume sampler operated mainly on solar power during the day time and electrical generator housed in the downwind direction during the night time. Daily helicopter operations were carried out from the embarked ship to the sampling site for the changing and collection of the filter set. LH is a more coastal site as it is located close to the open ocean and is separated by small islands and sea ice (varying from few meters to few kilometres) from the two permanent bases in this area, Zhongshan and Progress, which are almost 9 -10 km due northeast and the summer camp, Law Base (Australia) due east, According to the Committee on Environmental Protocol of the Antarctic Treaty System, the area is environmentally fragile and falls within Antarctic Specially Man-

aged Area No. 6 (ATCM Measure 2 (2007) Annex B). Since the mid-1980s, the Larsemann Hills region is on high environmental risk due to an extensive vehicular network, maintenance of an airstrip (Fig. 1), and the logistic activities of these research stations.



Fig 1: Study area

2. Material and Methods

Sampling of aerosols was carried out during 20th January to 3rd February 2009 at Larsemann Hills (LH) and 23rd February - 7th March 2009 near Maitri station at Schirmacher Oasis (SO), using a high volume sampler. The samples were collected over an average time period of 24 hrs (the sampling period varied between 18-32 hrs as per the weather conditions). The flow rate of the sampler was maintained at 1.2 lpm using a calibrated flow meter. The aerosols were collected over pre washed and pre combusted Quartz fibre filter paper to reduce any contamination and remove excess moisture. All operations were done by wearing particle-free gloves under clean conditions. The sampling site was located 300m upwind (in the direction of the incoming wind) of the station so that the samples are least affected by station activities such as incineration, vehicle movement, and operation of diesel generators, Even though extreme care was taken to operate the instrument away from local contamination, it could not be totally avoided near Maitri, where significant station activities persisted.

The filters were stored frozen in HDPE sealed bags and transported back to the onshore laboratory for analysis. Microwave assisted digestion was carried out using CEM (Mathews N.C USA) microwave Accelerated reaction system using a pressure controller and double walled lined vessels made from Teflon PFA. Wet digestion was carried out as per method described by Paudyn and Smith (1992). After the complete digestion the

samples were analyzed using a Thermo Elemental X7 Series inductively coupled plasma mass spectrometer (ICP-MS) with collision cell technology (CCT). All parts of the equipment/ tools that come in contact with the samples were cleaned with 2% ultra-pure HNO₃ and subsequently with Milli-Q Element water (18.7 MΩ) prior to the analysis. Ultrapure acids were prepared by sub-distillation of Merck AR acids using a PicoTrace Cupola sub-distillation system having TFM/PTFE lining. Although modern ICP-MS systems can analyze more than 40 elements, the concentration of elements available in the samples within the detection limits of the instrument was very restricted. Accordingly, only the following elements were studied here: Na, Li, K, Fe, V, Mn, Cr, Cu and Pb. Half of the filter was acid digested following an 8M HNO₃ + 2.9M HF digestion protocol (Planquette & Sherrell 2012) through a Microwave accelerated Reaction system (MARS). Clean protocols were strictly followed. The detection limits were estimated as three times the standard deviations of the blank. Most of the elements showed negative values except V, Cr and Mn, which were around the detection limits. The % RSD of Al, Li and Fe were found to be high during the study hence they were not considered in the data analysis except Na, Ca, Mg, K, and Al for which RF power was 500 W; nebulizer gas flow rate - 0.97 l/min; auxiliary gas flow rate - 0.90 l/min; and cool gas flow rate - 13.0 l/min. Fe and Se were analyzed using CCT. All sample and standard preparations were carried out inside a class ten PTFE-coated laminar bench and only freshly obtained Milli-Q Element water was used for all purposes. In order to calibrate and evaluate the measurement accuracy, Standard Reference Material NIST 1640 from National Institute of Standards and Technology was also used. The analytical precision obtained using the repeated analysis of NIST 1640 standard was excellent as follows: <10 % - Na, <5 % - Mo, Pb, Co, Sb, Sc,; and <2 %- Cr, Mn and Cu. All concentrations of elements are reported here in micrograms per liter.

3. Results and Discussion

3.1 Trajectory Analysis

To explore possible sources of the observed trace elements in aerosols, air mass back trajectories were performed at 100m, 500m and 1000m height above the ground over the sampling locations every 6 h, going backward 10 days. The trajectories were calculated from the National Oceanic and Atmospheric Administration Global Data Assimilation System meteorology database (Draxler & Rolph 2014), using the Hybrid Single-Particle Langrangian Integrated Trajectory (HYSPLIT) program. The trajectory

analysis revealed that during the study all the trajectories, arriving at the measurement sites, were confined to either inland region of Antarctica arriving from south and south east to the sampling sites and from northern coastal oceanic regions of Antarctica (Fig 2). No trajectories were observed to cross the circumpolar vortex to reach middle- to low-latitude regions or to the Southern Hemispheric continents (such as Australia, southern Africa, or South America). Further four blizzard events were also recorded during the study period, 2 at LH and 2 at SO. The two blizzard events observed at LH, 24th - 25th January and a more intense episode on 3rd - 4th Feb 2009. The two blizzard events at SO near Maitri, were comparably long and more intense, 28th - 29th February and 7th - 8th March 2009.

3.2 Elemental Composition of aerosols

The chemical compositions of the aerosols differ regionally, due to diverse wind regime, meteorological conditions, and the balance between marine and continental sources, and the distance to other source regions for long-range transport of anthropogenic pollutants. Na dominates the mass concentration of the elements forming 92% of the total elemental concentration. Na has not been included in the pie chart due to its high abundance which could mask the relative contributions from other elements.

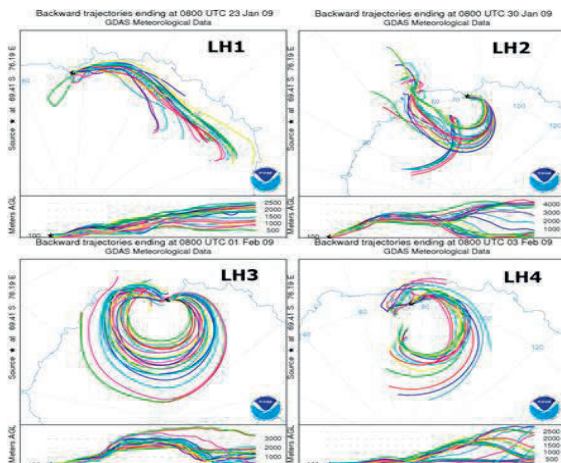


Fig 2 (a) 10 day back Trajectories arriving at the sampling site (Larsemann Hills) from three different heights (100m,500m,1000m) at a 6 hourly interval

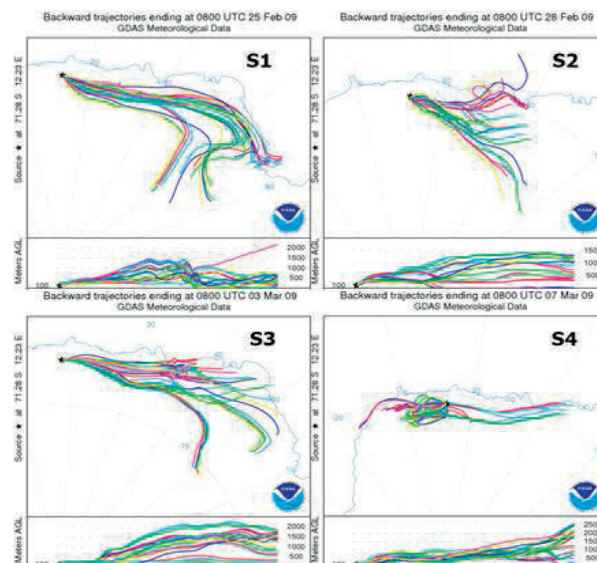


Fig 2(b) 10 day back Trajectories arriving at the 2nd sampling site (Schirmacher Oasis) from three different heights (100m,500m,1000m) at a 6 hourly interval

Cu, Cr and Mn were found to be the three most dominant elements in both the study areas. Therefore it is suggested that crustal contribution (Cr+Mn=65%) at LH was dominant in comparison to SO (Cr+Mn=51%). Cu was the most dominant element (38%) near Maitri station (Fig. 3). It was found to be of anthropogenic origin in many studies in Antarctic region (Toscano et al., 2005; Yuanhui et al., 2015) and specifically in the present study area (Thamban and Thakur., 2013). The contribution of Pb, Cu, Co to aerosols was two times higher near Maitri station as compared to LH region (Fig. 3). However Cd and Sb were slightly higher at LH. Mo contribution to the Antarctic coastal aerosols was almost equal in both the sampling areas. The prevailing winds arriving at SO and LH are mostly from the southeast direction during the study period, it is probable that there could be some influence from the station activities at these regions. The Novo station in SO and Zhongshan, Progress stations at LH are located in the south east direction from the sampling sites. The strong katabatic winds during the sampling time can influence the aerosols with anthropogenic station activities like operation of generators, boiler, incinerator-based toilets and vehicular (piston pulley, cranes and dozers) movement also including helicopters (during hovering, landing and take-off from helipads). Cd was found higher in coastal Antarctica as compared to concentration in aerosols over southern ocean suggesting some additional anthropogenic sources at the coast (Xu & Gao 2014). Analysis of trace metals in surface snow samples from Lambert glacier basin, close to (~80 km SW) the present study region

revealed that heavy metal distribution in this region are controlled by different transport and deposition mechanisms related to the physical and chemical alterations in the properties and sources of aerosol (Hur et al. 2007).

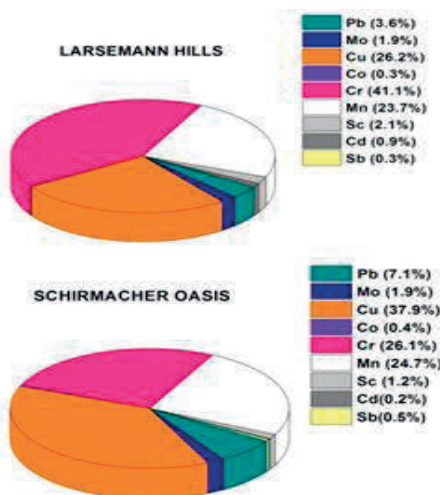


Fig 3: Contribution of trace elements in both the study areas

3.3 Enrichment Factors

Enrichment factor was used to differentiate between the different sources of aerosols. Crustal influences on aerosol element concentrations can be assessed by crustal enrichment factors (EFC) by normalizing by the reference crustal element. EFC are calculated according to following equation:

$$EFC_x = \frac{X/Ref\ X(aerosol)}{X/Ref\ X(crust)}$$

Where $X/Ref\ X(aerosol)$ is the ratio of the concentration of sample element "X" under consideration and the reference element (Al, Fe or Mn) in the aerosol sample. $(X/Ref\ X)_{crust}$ is their mean concentration ratio in upper crustal rocks (Wedepohl 1995). For the present study, we used Mn as the reference element. Many studies in Antarctica have designated Mn as a predominantly crustal element (Ikegawa et al., 1997, Ikegawa et al., 1999; Planchon et al., 2002; Hur et al., 2007) and stated that the variations of Mn were similar to those of Al. Also, (Wagenbach et al., (1988) utilized Mn as the reference element for crustal aerosol. Thus, EFC values from 1 to 10 may still indicate a crustal material source for the elements (Chester et al., 1991). The aerosol samples collected in Larsemann hills are marked as

LH1- LH4 and the samples collected in near Maitri Station in SO are marked as S1- S4 (Fig. 4). The average Efc of Co was <1 in both LH and SO, suggesting no significant enrichment. Similar observations were made at Terra Nova bay Antarctica (Toscano et al. 2005). The Efc of Sc ranged from 1-6 in both the regions suggesting a significant crustal source (Fig.4). Further the Efc of Pb showed a crustal source in Larsemann Hills (average Efc 7.8) but a slight anthropogenic influence in aerosols over SO (average Efc = 14.7). The enrichment factors of Cu, Mo, Cd, Sb were >10 indicating that these elements had anthropogenic sources in the study regions. The Efc of Cd was specifically higher (~ 300) in LH4 sample when the blizzard event was recorded at Larsemann Hills (Fig.4).

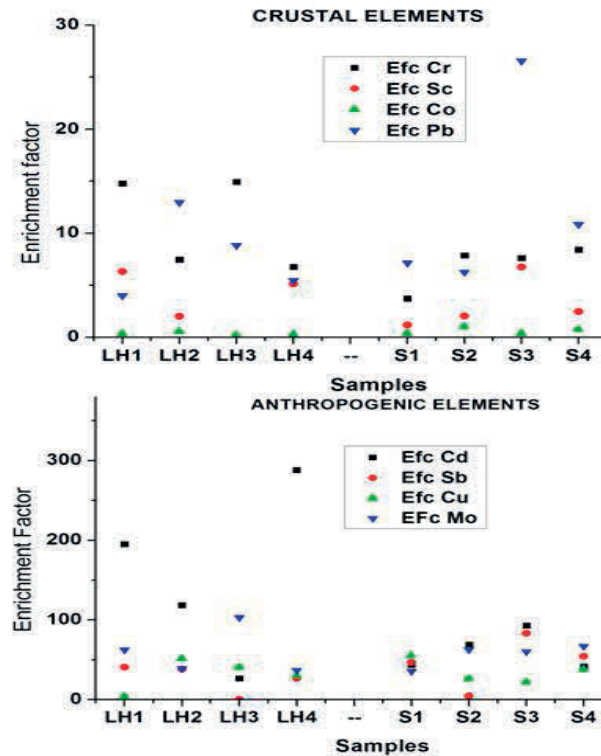


Fig 4: Enrichment factors

Efc of Cd was found high at the coastal Antarctic site in the study of Xu and Gao 2014 emphasising the contribution of Cd from anthropogenic and volcanic sources of Cd (Rädlein & Heumann 1995; Pacyna & Pacyna 2001) which needs to be further explored. Efc of Cu was found >10 even at geographic south pole Maenhaut et al. 1979). Trace elemental studies of aerosols in Terra Nova bay and great wall station, Antarctica also sug-

gested anthropogenic sources for Cu, Pb, Cd (Toscano et al. 2005; Yuanhui et al., 2015) were 4-9 orders of magnitude more than for marine sources as well as crustal sources. Chiavarini et al. (1994) reported that the most representative elements of the incinerator emissions were V, Cr, Cu, Zn, Cd, Sb supporting the observation of the present study. The trajectory analysis for larsemann hill region revealed that the LH1 and LH2 samples (23rd and 30th Jan 2009) were influenced by air mass travelling along the coast from east to west along the Antarctic coastline (Fig 2a) over the exposed rock outcrops. These samples revealed that EFcs of Co, Sc, Cr were within the range of 1-10. The trajectories during collection of the sample LH3 were from the southern inland region and travelled in a circular motion to reach back to the sampling site. The average windspeed on 30th January to 1st February 2009 (LH3) was noted to be 16m/s and was marked as the starting of the blizzard. The Efc of Co, Mn and Sc showed lowest value and Pb, Cu, Co showed high EFs in this sample. These observations suggest that the crustal elements do not show any significant enrichment during a blizzard event probably since the crustal elements are dominantly present in larger size particles in coastal Antarctica (Thakur and Thamban, 2014) tend to settle faster at high wind speed and the aerosol gets enriched by anthropogenic elements during such an event probably because the high wind picks up more fine particles from station activities, which do not settle as quickly as the coarse particles. When the aerosol samples of LH showed that Efc of Cr was >10 on S5 when the trajectory was influenced by air mass travelling from east where other stations (Zhongshan and Progress station) are based, it suggested the influence of mixed crustal and anthropogenic elements. Among the anthropogenic elements Efc of Mo was the highest supporting the anthropogenic influence of the stations situated on the east. High EFcs for all anthropogenic elements specifically Cd and Sb was observed on S3 (Blizzard event) when the air mass travelled from south east direction with the circular air mass movement. The average EF of Pb and Sb are 2 fold higher at LH as compared to SO suggesting more anthropogenic influence in aerosols of Schirmacher oasis.

4. Conclusion

The present study is a preliminary baseline study of trace metals present in the aerosols at two distinct Antarctic sites. The aerosols were found to be predominately marine as suggested by high Na concentration at both the sampling sites. The crustal influence was more at Larsemann hills in contrast to the anthropogenic influence near Maitri station in Schirmacher oasis. Co and Sc are the dominant crustal elements at both the sites. Pb in aerosols was mostly crustal-derived at Larsemann hills but anthropogenic over Schirmacher oasis. During blizzard events the aerosols were found

to be enriched with anthropogenic elements like Cd, Mo and Cu at both the sampling sites. This enrichment of aerosols with trace elements during blizzard events could be of important implications since one event can deposit 2-3 fold higher concentrations of trace elements on the snow since blizzards are often accompanied by snow fall and snow drift. Further the rocky outcrops of Larsemann hills play a significant role in generating coarse crustal aerosols enriched with Co, Cr and Pb. Maitri can be regarded as a continental station under moderate anthropogenic influence from local station activities while LH was rather pristine and is more influenced by local marine and crustal sources during Antarctic summer. The trace elemental concentration of aerosols at Larsemann hills during this study represents the baseline data of the site, before the station building activities commenced in 2010. This data is very crucial for any future aerosol studies conducted at Larsemann hills, since the Third Indian Permanent station; Bharati has been commissioned in 2012. Therefore to investigate into the trace metal chemistry of aerosols after the station was commissioned, a detailed sampling of size segregated aerosols has been carried out for a period of 30 days at Larsemann hills in the 33rd Indian Antarctic Expedition. The results would be compared with the data and findings of this study to draw out a comprehensive understanding of the human interferences at coastal Antarctica.

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REFERENCES

- ARIMOTO, R., DUCE, R.A., RAY, B.J.&UNNI, C.K. 1985. Atmospheric trace elements at Enewetak Atoll: 2. Transport to the ocean by wet and dry deposition. *Journal of Geophysical Research*, 90, 2391, doi: 10.1029/JD090iD01p02391.
- ARIMOTO, R., DUCE, R. A., RAY, B.J., HEWITT, A.D.&WILLIAMS, J. 1987. Trace elements in the atmosphere of American Samoa: Concentrations and deposition to the tropical South Pacific. *Journal of Geophysical Research*, 92, 8465, doi: 10.1029/JD092iD07p08465.

- ARIMOTO, R., ZENG, T., DAVIS, D., WANG, Y., KHAING, H., NESBIT, C. & HUEY, G. 2008. Concentrations and sources of aerosol ions and trace elements during ANTICI-2003. *Atmospheric Environment*, doi: 10.1016/j.atmosenv.2007.05.054.
- ARTAXO, PAULO., RABELLO, MARTA., MAENHAUET, WILLY., GRIEKEN, R. VAN. 1992. Artaxo.pdf. *Tellus B*, 44, 318-334.
- CHESTER, R., BERRY, A.S AND MURPHY, K.J.T. 1991. The distribution of particulate atmospheric trace metals and mineral aerosols over the Indian Ocean. *Marine Chemistry*, 34, 261-290
- CHIAVARINI, S., GALLETTI, M., MICHETTI, I., PERINI, A., & TESTA, L., 1994. Environmental Monitoring at Terra Nova Bay Station From 1989 to 1991, *International journal of environmental Analytical chemistry*, 55, 331-240.
- DRAXLER, R.R. & ROLPH, G.D. 2014. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (<http://www.arl.noaa.gov/HYSPLIT.php>). NOAA Air Resources Laboratory, College Park, MD. NOAA Air Resources Laboratory.
- DUCE, R. A, HOFFMAN, G.L. & ZOLLER, W.H. 1975. Atmospheric trace metals at remote northern and southern hemisphere sites: pollution or natural? *Science (New York, N.Y.)*, 187, 59-61, doi: 10.1126/science.187.4171.59.
- EISELE, F., DAVIS, D.D., ET AL. 2008. Antarctic Tropospheric Chemistry Investigation (ANTCI) 2003 overview. *Atmospheric Environment*, 42, 2749-2761, doi: 10.1016/j.atmosenv.2007.04.013.
- GASPARON, M. & MATSCHULLAT, J. 2006. Geogenic sources and sinks of trace metals in the Larsemann Hills, East Antarctica: Natural processes and human impact. *Applied Geochemistry*, 21, 318-334, doi: 10.1016/j.apgeochem.2005.09.013.
- HARA, K., OSADA, K., ET AL. 2004. Chemistry of sea-salt particles and inorganic halogen species in Antarctic regions: Compositional differences between coastal and inland stations. *Journal of Geophysical Research D: Atmospheres*, 109, 1-18, doi: 10.1029/2004JD004713.
- HUR, S., DO, CUNDE, X., ET AL. 2007. Seasonal patterns of heavy metal deposition to the snow on Lambert Glacier basin, East Antarctica. *Atmospheric Environment*, 41, 8567-8578, doi: 10.1016/j.atmosenv.2007.07.012.
- IKEGAWA, M., KIMURA, M., HONDA, K., MAKITA, K., FUJII, Y. & ITOKAWA, Y. 1997. Springtime peaks of trace metals in Antarctic snow. *Environmental Health Perspectives*, doi: 10.1289/ehp.97105654.
- IKEGAWA, M., KIMURA, M., ET AL. 1999. Geographical variations of major and trace elements in East Antarctica. *Atmospheric Environment*, 33, 1457-1467, doi: 10.1016/S1352-2310(98)00243-X.
- JOURDAIN, B., PREUNKERT, S., CERRI, O., CASTEBRUNET, H., UDISTI, R. & LEGRAND, M. 2008. Year-round record of size-segregated aerosol composition in central Antarctica (Concordia station): Implications for the degree of fractionation of sea-salt particles. *Journal of Geophysical Research Atmospheres*, 113, 1-9, doi: 10.1029/2007JD009584.
- LAMBERT, G., ARDOUIN, B. & SANAK, J. 1990. Atmospheric transport of trace elements toward Antarctica. *Tellus*, 42B, 76-82.

- LEGRAND, M., SCIARE, J., JOURDAIN, B., AND GENTHON, C. 2001. Subdaily variations of atmospheric dimethylsulfide, dimethylsulfoxide, methanesulfonate, and non-sea-salt sulfate aerosols in the atmospheric boundary layer at Dumont d'Urville (coastal Antarctica) during summer, *Journal of Geophysical Research*, 106, 409-414.
- MAENHAUT W., ZOLLER W.H., DUCE R.A. & HOFFMAN G.L. 1979. Concentration and size distribution of particulate trace elements in the south polar atmosphere. *Journal of Geophysical Research*, 84, 2421-2431.
- MAENHAUT, W., RAEMDONCK, H., SELEN, A., VAN GRIEKEN, R AND WINCHES-TER, J.W. 1983. Characterization of the atmospheric aerosol over the eastern equatorial Pacific. *Journal of Geophysical Research*, 88, 5353-5364.
- MISHRA, V.K., KIM, K.-H., HONG, S. & LEE, K. 2004. Aerosol composition and its sources at the King Sejong Station, Antarctic peninsula. *Atmospheric Environment*, 38, 4069-4084, doi: 10.1016/j.atmosenv.2004.03.052.
- MOURI, H., NAGAO, I. & KOGA, S. 1997. Elemental compositions of individual aerosol particles collected over the Southern Ocean?: A case study. *Atmospheric Research*, 43, 183-195.
- PACYNA J.M. & PACYNA E.G. 2001. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. *Environmental Reviews* 9, 269-298.
- PLANQUETTE, H. & SHERRELL, R.M. 2012. Sampling for particulate trace element determination using water sampling bottles: methodology and comparison to in situ pumps. *Limnology and Oceanography: Methods*, 10, 367-388, doi: 10.4319/lom.2012.10.367.
- PLANCHON, F. A. M., BOUTRON, C. F., BARBANTE, C., COZZI, G., GASPERI, V., WOLFF, E. W., et al. 2002. Changes in atmospheric heavy metals in Antarctic snow from Coats Land since the mid-nineteenth century. *Earth and Planetary Science Letters*, 200(1-2), 207-222.
- RADLEIN N. & HEUMANN K.G. 1995. Size fractionated impactor sampling of aerosol particles over the Atlantic Ocean from Europe to Antarctica as a methodology for source identification of Cd, Pb, Tl, Ni, Cr, and Fe. *Journal of Analytical Chemistry*, 352, 748-755.
- SAVOIE, D. L., PROSPERO, J. M., LARSEN, R. J., HUANG, F., IZAGUIRRE, M. A., HUANG, T., SNOWDON, T. H., CUSTALS, L., AND SANDERSON, C. G. 1993. Nitrogen and sulfur species in Antarctic aerosols at Mawson, Palmer Station, and Marsh (King George Island), *Journal of Atmospheric Chemistry*, 17, 95-122.
- SAXENA V.K. & RUGGIERO F.H. 2013. Aerosol measurements at Palmer Station, Antarctica. In C.R. Bentley (ed.): *Contributions to Antarctic Research I. Antarctic Research Series 50*. Pp. 1-5. Washington, DC: American Geophysical Union.
- THAKUR, R.C & THAMBAN, M. 2014. Latitudinal and size segregated ionic variability of aerosols over the Indian and Southern Ocean during 2010 summer, *Aerosols and Air Quality Research*, 14, 220-236.
- THAMBAN, M. & THAKUR, R.C. 2013. Trace metal concentrations of surface snow from Ingrid Christensen Coast, East Antarctica--spatial variability and possible anthropogenic contributions. *Environmental monitoring and assessment*, 185, 2961-2975, doi: 10.1007/s10661-012-2764-0.

- THAMBAN, M., LALURAJ, C.M., MAHALINGANATHAN, K., REDKAR, B.L., NAIK, S.S.&SHRIVASTAVA, P.K. 2010. Glaciochemistry of surface snow from the Ingrid Christensen Coast, East Antarctica, and its environmental implications. *Antarctic Science*, 22, 435-441, doi: 10.1017/S0954102010000155.
- TIN, T., FLEMING, Z.L., ET AL. 2009. Impacts of local human activities on the Antarctic environment. *Antarctic Science*, 21, 3-33, doi: 10.1017/S0954102009001722.
- TOSCANO, G., GAMBARO, A., MORET, I., CAPODAGLIO, G., TURETTA, C.&CESCON, P. 2005. Trace metals in aerosol at Terra Nova Bay, Antarctica. *Journal of environmental monitoring*: JEM, 7, 1275-1280, doi: 10.1039/b507337p.
- UDISTI, R., DAYAN, U., ET AL. 2012. Sea spray aerosol in central Antarctica. Present atmospheric behaviour and implications for paleoclimatic reconstructions. *Atmospheric Environment*, 52, 109-120, doi: 10.1016/j.atmosenv.2011.10.018.
- WAGENBACH, D., GÖRLACH, U., MOSER, K.&MÜNNICH, K.O. 1988. Coastal Antarctic aerosol: the seasonal pattern of its chemical composition and radionuclide content. *Tellus B*, 40B, 426-436, doi: 10.1111/j.1600-0889.1988.tb00114.x.
- WEDEPOHL, K.H. 1995. Ingerson Lecture: The composition of the continental crust. *Geochimica et Cosmochimica Acta*, 59, 1217-1232, doi: 10.1016/0016-7037(95)00038-2.
- WELLER, R., MINIKIN, A., WAGENBACH, D., AND DREILING, V. 2011. Characterization of the inter-annual, seasonal, and diurnal variations of condensation particle concentrations at Neumayer, Antarctica. *Atmospheric Chemistry and Physics*, 11, 13243-13257, doi:10.5194/acp-11-13243-2011.
- WELLER, R. AND WAGENBACH, D. 2007. Year-round chemical aerosol records in continental Antarctica obtained by automatic samplings, *Tellus*, 59B, 755-765.
- WEISEL, C. P., DUCE, R. A., FASHING, J.L AND HEATON R.W.1984. Estimates of the transport of trace metals from the ocean to the atmosphere. *Journal of Geophysical Research*, 89,11607-11611.
- WOLFF, E.W., SUTTIE, E.D.&PEEL, D.A. 1999. Antarctic snow record of cadmium, copper, and zinc content during the twentieth century. *Atmospheric Environment*, 33, 1535-1541, doi: 10.1016/S1352-2310(98)00276-3.
- XU, G.&GAO, Y. 2014. Atmospheric trace elements in aerosols observed over the Southern Ocean and coastal East Antarctica. *Polar Research*, 33, 1-16, doi: 10.3402/polar.v33.23973.
- YUANHUI, Z., YANMIN, W., ET AL. 2015. Seasonal variations in aerosol compositions at Great Wall Station in Antarctica. 26, 196-202, doi: 10.13679/j.advps.2015.3.00196.
- ZOLLER, W.H., GLADNEY, E.S.&DUCE, R. A. 1974. Atmospheric concentrations and sources of trace metals at the South pole. *Science*, 183, 198-200, doi: 10.1126/science.183.4121.198.
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