Distribution of major and minor elements in the surface water of Southern Ocean near east Antarctica

Pawan Kumar Bharti*, Bhupesh Sharma, Narendra Pal, R. K. Singh and A. K. Tyagi
Antarctica Laboratory, R & D Division, Shriram Institute for Industrial Research, 19, University Road, Delhi-110 007, India.

*Correspondence e-mail:gurupawanbharti@rediffmail.com

Original Article

Abstract

Distribution of major and minor element concentrations in Antarctic surface seawater samples was evaluated. Seawater samples were collected from eight sampling location in Southern Ocean from latitude S 67º16´10.9´´ and longitude E 28º39´64.5´´ to latitude S 69º17´42.9´´ and longitude E 76º13´23.3´´ and analyzed for various heavy metals like copper (Cu), lead (Pb), cadmium (Cd), zinc (Zn), nickel (Ni), chromium (Cr). The concentrations of heavy metals Cu, Pb, Cd, Zn, Ni, Cr and other major elements like sodium, potassium, calcium, magnesium, boron were measured in selected seawater samples using Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES). Spatial difference of the heavy metal concentrations in Antarctic seawater was negligible and their concentrations were in the order of Fe > Zn > Cu > Mn > Co > Pb > Ni > Cd.

The total concentrations of all selected metals were found slightly fluctuated in coastal water of east Antarctica. The results indicated that the concentrations of metals in seawater were found uniformly in entire selected stretch of Southern Ocean. Sodium, potassium, calcium, magnesium, boron and iron metals were found as the dominant constituents among the sea water contents. Aluminum (0.3-15.0 μg/cc), zinc (0.27-1.9 μg/cc), copper (0.04-0.23 μg/cc) and molybdenum (0.10-0.77 μg/cc) were also found in sufficient concentrations in all seawater samples. Strontium was also one of the dominant alkaline earth metals in sea water. However, the concentration of strontium (22.8-53.0 μg/cc) was found to be evenly distributed from Indian Bay to Larsemann Hills in east Antarctica. Selenium and chromium were the rarest metals in seawater as these were below detection limit in all samples.

Keywords: Metals, seawater, Antarctica, Southern Ocean.

Introduction

Processes which control the distributions and variability of trace elements especially metals in coastal zones remain poorly understood due to the lack of strong research setups and networks. Existing knowledge of most continental shelf waters is sufficient only to establish that nearshore trace metal concentrations are usually elevated relative to open ocean waters at similar depths, reflecting both natural and anthropogenic inputs at the ocean margins (Paul Field *et al.*, 1999; Bruland and Franks, 1983). The limited understanding of the chemical variability in coastal waters is due in part to data limitations by laborious and slow analytical procedures and techniques for metals in seawater. These understandings are relatively less common in some less explored and pristine environments like southern ocean.

Our understanding of the biogeochemical cycles of trace elements and their influence on the oceanic ecosystem of the Southern Ocean is still limited, with perhaps the exception of iron (Boyd *et al.*, 2007). Certain trace metals have profiles that are nutrient-like, like cadmium (Cd) and copper (Cu), which are indicative of their involvement in biological cycles (Boyle, 1988). In contrast, other metals have a scavenged-type behaviour like lead (Flegal and Patterson, 1983) or behave in a conservative manner like uranium (Bruland and Lohan, 2003). Elements such as manganese (Mn) can be considered hybrid-type metals at high latitudes, as their distribution is controlled by both biological uptake and scavenging processes (Bruland and Lohan, 2003). Furthermore, the oceanic behaviour of other trace metals like silver (Ag) is still not well understood, with little data on Ag distributions in the global ocean, notably in the Southern Hemisphere (Zhang *et al.*, 2004). Despite major advances on the ecological involvement of trace metals and their geochemical dynamics in the ocean, basic knowledge is still lacking on their biogeochemical cycles. For instance, there are only a few comprehensive datasets of Mn (Middag *et al.*, 2011), and of Cu, Cd and Pb (Ellwood, 2008) for the Southern Ocean. The external sources of trace metals to the southeastern Atlantic and the Southern Ocean are not well constrained. Recent work suggests the importance of advection of water masses enriched in trace metals following contact with continental margins (Bown *et al.*, 2011; Chever *et al.*, 2010), in addition to atmospheric depositions to surface waters and inputs from hydrothermal vents to bottom waters (Klunder *et al.*, 2011). The coupling between trace and major nutrients cycles, such as the correlations between Cd and phosphate (PO_4) in the Southern Ocean (Elderfield and Rickaby, 2000), indicates the removal of trace nutrients in surface waters due to phytoplankton uptake and their later sinking and remineralisation in deep waters. However, our knowledge of this coupling is still limited to a small number of trace elements (Boye, 2012).

Some literature concerning heavy metals in the snow, ice, seawater, atmosphere, soil, rock and animals in the Antarctic region has been published (Bharti *et al.*, 2015; Honda *et al.*, 1987; Bharti and Gajananda, 2015; Bharti *et al.*, 2016). However, analytical data on the Antarctic marine ecosystem including the seawater and biological materials for understanding the detailed distribution and bioaccumulation processes of heavy metals are rather scarce (Yamamoto *et al.*, 1987a; Chiarelli and Roccheri, 2014).

The Antarctic marine ecosystem, especially beyond south of the Antarctic convergence, is stable and old and has a higher percentage of endemic species: thus it is simple in comparison with otherecosystems. Since the atmospheric mixing between north and south of the Antarctic convergence is very slow, the Antarctic area is a comparatively closed environment (Knox, 1970). Aquatic systems such as the seawater, inland water, etc. are important stages in the biogeochemical cycle. Although dissolved levels are usually in the trace range of 10^{-6}-10^{-9} M l^{-1} they remain significant, because they enter into the food chain and interactions with suspended particulate and sediments largely occur via the dissolve state (Bruland and Lohan, 2003).

In environmental research, toxic metals particularly Cd, Pb, Ni, Cr, etc. are becoming increasingly significant owing to their biological non-degradability and chronic toxicity results from their accumulation in vital organs of humans. The various heavy metals in seawater become toxic if present in excessive quantities and pose a potential threat to the ecosystem. Therefore, there has been constant effort to measure the impact of these metals on fauna (Bharti and Singh, 2013; De Silva, 1997).Trace metals in seawater, although present in very low concentrations, have a profound influence on marine biogeochemistry and function as critical indicators of fundamental processes. However, given the lower concentrations of many of the analytes of interest and a generally poor understanding of speciation within the matrix, chemical analysis of seawater is uniquely difficult. Potential interference from total dissolved solids often prevents accurate determination of the ambient levels of trace metals, making most traditional analytical method ineffective.

Few researchers are engaged in monitoring and assessment work especially on metal detection in water bodies and have done some work in this regards (Bharti 2012a; Bharti and Singh, 2013; Bharti *et al.*, 2014; Bharti and Niyogi, 2015a; Bharti and Niyogi, 2015b; Bharti and Niyogi, 2015c;Bharti and Gajananda, 2015; Bharti *et al.*, 2016). The objective of the research work is to identify, evaluate and predict the impact of increasing anthropogenic activities on environmental components of Antarctica. The generated data may reveal some interrelations of geo-genic and anthr`opogenic activities in natural aquatic ecosystem. Selection of such a huge sampling stretch and its planned sampling and analysis work will disclose some relationship between some elements and their availability, movement and distribution in the earth ecosystem. On the other hand, the outcome this work will compensate and try to envelop the gaps in research work in this particular area of analytical research.

Material and methods

Study area

Environmental monitoring and impact assessment studies were carried out in Antarctica during the austral summer seasons of various Indian Scientific Expeditions to Antarctica (Bharti, 2012b). Long voyage from Goa (India) to Cape Town (South Africa) and further to east Antarctica (Maitri station to Bharati

station) provides an opportunity to find out and evaluate the surface seawater quality of entire Southern Ocean stretch from Indian Bay to Larsemann Hills aboard Russian M/V Emerald Sea. Southern Ocean was selected as a study site for the present study.

The surface seawater samples were collected from Indian Bay (near Maitri station, Queen Maud Land) to Bharti station (Larsemann Hills, Ingrid Christenson Coast) in the Southern Ocean during the XXVII Indian Scientific Expedition to Antarctica (ISEA). Eight sampling points were selected at various locations, namely S-41, S-43, S-45, S-47, S-49, S-51, S-53 and S-55 from Indian bay to Larsemann hills in east Antarctica and the collected samples were analysed for the major elements and trace metal concentrations in surface sea water. The location map of study area and sampling stretch in the Southern Ocean is given in Fig.1. Geo-coordinates of all sampling points are given in Table1.

Sampling

The sampling of surface seawater was carried out during the voyage at an interval of approximately 6 or 8 degree
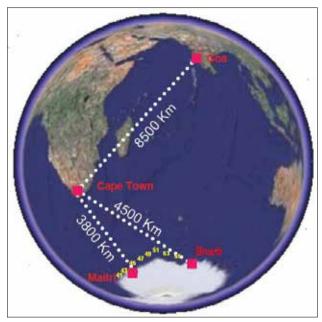

Fig. 1. Location map and sampling stretch in Southern Ocean (Location cited as 41-55 are the actual sampling station)

Table 1. On-spot data of seawater samples collected from Southern Ocean

S.N.	Samples Code	Date	Time	Latitude	Longitude	pH	Temperature (ºC)
1	S-41	17.02.08	12.15	S 67°16′10.9″	E 28°39′64.5″	8.0	-0.8
2	S-43	18.02.08	10.00	S 66°14′27.6″	E 36°41′36.9″	7.8	-0.5
3	S-45	19.02.08	07.25	S 65°21′29.3″	E 43°21′01.7″	7.7	-0.6
4	S-47	20.02.08	8.25	S 63°42′10.9″	E 52°11′64.5″	8.0	-0.8
5	S-49	21.02.08	07.36	S 65°32′41.7″	E 58°05′56.5″	8.0	-1.5
6	S-51	22.02.08	07.23	S 66°11′32.0″	E 68°49′03.6″	7.3	-0.6
7	S-53	23.02.08	06.40	S 67°23′12.0″	E 73°29′50.5″	7.8	-1.0
8	S-55	24.02.08	06.36	S 69°17′42.9″	E 76°13′23.3″	7.2	-0.9

difference in the longitude. Sampling vessel, rope, sampler's hands were disinfected using IPA to avoid the contamination. The samples were collected in the Gamma irradiated, clean and sterilized PET bottles. As per the standard specifications, an appropriate quantity of Sodium thiosulphate was also placed in the PET bottles to avoid the chlorine contamination. Collected seawater samples were immediately filtered through a 0.45 pm membrane filter using a vaccum filtration apparatus and stored in vertical position maintaining the temperature 1–4°C with ice pack enveloped conditions immediately after preservation by 1 ml 70 % HNO3. The samples were transported to the laboratory using ice boxes after completion of expedition and analyzed for the major elements and trace metals. Aseptic conditions were maintained during the collection of samples. The samples were kept in an ice pack to prevent any contamination of any foreign material or microbial flora of the samples during the transportation.

Analytical methods

Using a deliberate combination of oxidation, reduction, precipitation, extraction, chelation, filtration and concentration processes, trace metals can be precisely measured in seawater (Milne *et al.*, 2010). Depending upon the analyte of interest, seawater is then analysed using hydride generation atomic fluorescence spectroscopy (HG-AFS), Induced coupled plasma mass spectrometry (ICP-MS), or cold vapour atomic fluorescence spectrometry (CV-AFS) up to very low detection limits (Nielson and Sanders, 1983). Standard methods as described in APHA (2005) were followed for the dilution and analysis of various elements.

The analytical method used in this study was obtained from the modification of the one described by Jerez *et al.* (2010). The elements were determined by optical emission spectrometry with inductively coupled plasma (ICP-OES). All of the reagents used were of Analytical grade (Merck) and the water was

double-distilled and deionized (Milli-Q system, Millipore, USA). The analytical precision was verified by using blanks of every five samples, initial calibration by CWW-TM-D certified reference standards. The detection limit values, the reference material values and the percentage of reliability for each element were also calculated accordingly.

The detection limit of each element was calculated by using the formula; $DL = 3sB/a$ (DL: detection limit; sB: standard deviation of the number of counts corresponding to zero on the calibration line; a: the constant of the calibration line).

Results and discussion

The primary analyses of seawater were performed just prior to the beginning of the 19th century in laboratories. However, problems arised from changes in chemical composition through evaporation, biological activity or chemical interactions with the containing vessel, forced the marine chemist to transfer his laboratory from land to ships. Today, there is a strong and necessary trend toward using instrumental techniques, as opposed to the classical methods, especially when assaying very small amounts of materials (Bloom and Crecelius, 1984). Temperature and pH of sea water samples were recorded on spot and are given in Table-1. The seawater temperature recorded was sub-zero (range -0.5 to -1.5ºC) and the pH ranged from 7.2 to 8.0 from Maitri station to Bharti station.

Major elements

Sodium, potassium, calcium, magnesium, boron and iron metals were found to be the dominant constituents among the sea water contents (Table 2). Maximum sodium was found to be 54750.45 μg/cc at S-45site and minimum was 39670.45 μg/cc at S-49. Maximum potassium was found to be 2619.17 μg/cc at S-45 site and minimum was 2072.29 μg/cc at S-49 sampling pont. Maximum calcium was found to be 2258.12 μg/cc at S-45 site and minimum was 1642.15 μg/cc at S-49. Maximum magnesium was found to be 5987.13 μg/cc at S-45 sampling station and minimum was 4398.0 μg/cc at S-49. Maximum boron was found to be 109.23 μg/cc at S-47 site and minimum was 8.96 μg/cc at S-49. Maximum Iron concentration was found to be 30.69 μg/cc at S-43 site and minimum was 1.3 μg/cc at S-55 near Bharti station at Larsemann Hills.

Besides these, aluminum (0.397–15.03 μg/cc) and zinc (0.273–1.9 μg/cc) were also present in significant quantities in all seawater samples.

Metals

Cadmium was found only in one sample near Maitri station as well as in one sample near Bharti station, which shows the doubtful distribution concept over cadmium introduction into sea ecosystems. Maximum cadmium was found to be 0.061

Table 2. Quantities of major constituents in seawater samples collected from Southern Ocean (values in μg/cc)

S.N.	Samples	Al	B	Ca	Fe	K	Mg	Na	Zn
1	S-41	15.031	22.839	1874.151	14.708	2294.668	5161.877	47149.200	1.178
2	S-43	3.291	24.392	2149.401	30.695	2596.668	5947.127	52554.200	1.113
3	S-45	0.922	12.759	2258.138	16.770	2619.168	5987.127	54750.450	0.465
4	S-47	1.592	109.229	1767.651	13.845	2248.543	4972.377	45400.450	0.813
5	S-49	1.055	8.966	1642.151	10.445	2072.293	4398.002	39670.450	0.315
6	S-51	0.397	11.500	2022.901	10.195	2530.043	5620.627	52916.700	0.273
7	S-53	0.844	26.642	2128.526	14.820	2539.418	5740.377	53267.950	1.900
8	S-55	4.944	13.723	1652.026	1.258	2128.543	4761.377	43052.950	0.503
Detection Limit		0.018	0.009	0.025	0.15	0.1	0.02	0.015	0.015

Table 3.Quantities of trace metals in seawater samples collected from Southern Ocean (values in μg/cc)

S.N.	Samples	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	Se
1	S-41	BDL	BDL	BDL	0.235	0.059	0.103	BDL	BDL	BDL
2	S-43	0.061	0.123	BDL	0.206	0.074	0.186	BDL	BDL	BDL
3	S-45	BDL	BDL	BDL	0.088	0.030	0.338	BDL	BDL	BDL
4	S-47	BDL	BDL	BDL	0.043	0.030	0.363	BDL	BDL	BDL
5	S-49	BDL	BDL	BDL	0.073	0.023	0.541	BDL	BDL	BDL
6	S-51	BDL	BDL	BDL	0.091	0.011	0.416	BDL	1.240	BDL
7	S-53	0.036	0.032	BDL	0.163	0.032	0.771	BDL	BDL	BDL
8	S-55	BDL	BDL	BDL	0.160	0.026	0.516	0.160	1.128	BDL
Detection Limit		0.027	0.06	0.022	0.02	0.002	0.16	0.08	0.29	1.5

μg/cc at S-43 site and 0.036 μg/cc at S-53, whereas it was found below detection limit in all remaining samples (Table 3). Similar trend was observed for cobalt metal in seawater samples collected from coastal regions of Southern Ocean. Maximum cobalt was found to be 0.123 μg/cc at S-43 site and 0.032 μg/cc at S-53, while it was found below detection limit in all remaining samples.

Chromium concentration was below detection level in all seawater samples. Selenium was also below detection level in all samples. Lead was present in only two samples collected from S-51(1.24 μg/cc) and S-55 (1.128 μg/cc). Nickel was also one of the rarest metals in seawater as it was detected in only one sample at site S-55 (0.16 μg/cc). Beside these, copper (0.043 – 0.235 μg/cc), manganese (0.011–0.074 μg/cc) and molybdenum (0.103–0.771 μg/cc) were also present in all seawater samples in trace quantities. Few metals are biologically essential to living organisms in trace quantities in sea ecosystem. These trace metals may re-circulate from sediment and became available for biota (Campbell *et al.*, 1988).

Dispersion of other constituents and spot values from Maitri to Bharti station

A slight variation was found in the total concentrations of metals at almost all sampling locations. The results indicated that the concentrations of metals in seawater were almost uniformly distributed in selected Southern Ocean stretch without any tremendous fluctuations. Aluminum (0.397 – 15.03 μg/cc), zinc (0.273 – 1.90 μg/cc), molybdenum (0.103 – 0.771 μg/cc) and copper (0.043 – 0.235 μg/cc) were also found in sufficient concentrations in all seawater samples. Arsenic, barium and phosphorous were not detected at sampling site S-55 (Table 4). Strontium was also found as one of the dominant alkaline earth metals in sea water samples and it ranges from 22.88 μg/cc to 53.0 μg/cc. However, the concentration of strontium was found to be evenly distributed in the selected stretch of Southern Ocean from Maitri to Bharti station in east Antarctica.

Highest value of sodium, potassium, magnesium and calcium

Table 4. Other important constituents in seawater samples collected from Southern Ocean (values in μg/cc)

S.N.	Samples	As	Ba	P	Sr
1	S-41	BDL	0.712	BDL	31.875
2	S-43	BDL	0.136	BDL	22.875
3	S-45	BDL	BDL	BDL	53.000
4	S-47	1.571	0.027	BDL	29.625
5	S-49	BDL	0.090	BDL	29.375
6	S-51	BDL	0.041	BDL	34.500
7	S-53	BDL	0.017	0.213	33.625
8	S-55	BDL	BDL	BDL	33.875
	Detection Limit	1.5	0.02	0.4	0.01

(BDL- Below Detection Limit)

metals was found at S-45 site in Southern Ocean. This trend shows the minimum turbulence and storage tendency of constituents in seawater. Temperature may also play an important role to regulate this functioning in sea ecosystem. All the metals and trace elements were observed almost uniformly available in the surface seawater from Maitri to Bharti station over east Antarctica. Some inputs may arise from the outer environment due to the anthropogenic reasons (MMS, 1988; Bharti, 2012c). Strontium is one of the widely distributed elements and the present trend can indicate the presence of natural sources of strontium in the vicinity. As per the observation, strontium sources may occur in coastal regions of Antarctica or in Southern Ocean. Spot values of different metals in sea stretch from Maitri Station to Bharti Station, east Antarctica shows very smooth distribution trends in Southern Ocean. However, water temperature and stagnancy may influence over heavy metals dispersions and many characteristics of seawater including biogeochemical cycle of microelements in Southern Ocean (Honda *et al.*, 1987; Boye *et al.*, 2012).

Acknowledgements

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