Metal quantification in surface water of Indian Ocean from India to South Africa

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Abstract

Water samples were collected from Indian Ocean and South Africa from latitude N 09°22'48.2" and longitude E 67°07'45.5" to Latitude S 34°54'37.7" and Longitude E 21°03'58.2" and analyzed for various metals like copper (Cu), lead (Pb), cadmium (Cd), zinc (Zn), nickel (Ni), chromium (Cr). The concentrations of metals Cu, Pb, Cd, Zn, Ni and Cr were measured using (ICP-OES) Inductively Coupled Plasma Optical Emission spectroscopy.

The total concentrations of metals were found in higher ranges in coastal water and were found to fluctuate with the spatial variations. The results indicated that the concentrations of metals in seashore were higher than those in inner ocean. Sodium, potassium, calcium, magnesium, boron and iron were found as the dominant elements among the sea water constituents. Aluminum, zinc, phosphorous and arsenic elements were also found in significant concentrations in all seawater samples. Strontium was one of the dominant alkaline earth metals in sea water. However, the concentration of strontium was found to be gradually deceasing from Goa to South Africa. Nickel was one of the rarest metals in seawater as it was found below detection level in all samples.

Keywords: Metals quantification, Seawater, South Africa, Indian Ocean.

Introduction

The inadequate awareness on the chemical fluctuations in the waters of seashore and oceans is due in part to data limitations by painstaking, hard and sluggish analytical techniques and procedures for the detection of metals. These considerations are comparatively less common in some less discovered and pristine ecosystems like southern ocean.

Understanding on the biogeochemical cycles of trace elements and their impact on the ecosystem of Southern Ocean is still inadequate with possibly the exclusion of iron[1]. Certain trace metals have profiles that are nutrient like e.g. cadmium (Cd) and copper (Cu), which are symptomatic of their contribution in biological cycles[2]. Aquatic systems such as the inland water, seawater etc. are important junctures in the biogeochemical cycle.

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Although dissolved levels of these elements are usually in the trace range of 10^{-6}-10^{-9} Ml^{-1} which remain significant, because they enter into the food chain and interactions with suspended particulate and sediments principally arise via the dissolved state[3].

In environmental research, toxic metals particularly Cd, Pb, Ni, Cr etc. are enticing progressively signification owing to their biotic non-degradability and chronic toxicity outcomes from their accumulation in important organs of humans. Several heavy metals in seawater become noxious if existent in extreme quantities and pose a potential peril to the ecosystem. Therefore, there has been continual effort to measure the influence of these metals on fauna[4].

Although trace metals in seawater are present in very low concentrations from estuaries to the Deep Ocean they have an insightful influence on oceanic biogeochemistry and function as precarious indicators of essential processes. However, given the lower concentrations of many of the analytes and a usually deprived indulgent of speciation within the matrix, chemical examination of seawater is exceptionally challenging. Probable interference from dissolved solids (salts) often checks precise determination of the ambient levels of trace metals creating most traditional analytical method futile and ineffective.

Few researchers are involved in environmental monitoring and assessment work especially on metal detection in various water bodies and have executed several works in this domain[5-14].

The major aim of the investigation is to identify, evaluate and predict the impact of accumulative anthropogenic activities on environmental components of Antarctica. The generated data may disclose some interrelations of geo-genic and anthropogenic accomplishments in natural aquatic ecosystem. Selection of such a big sampling stretch along with its planned sampling work and analysis results will disclose some correlation between several elements (metals) their availability, movement and distribution in the earth ecosystem. On the other hand, the outcome of this research work will compensate and try to wrap the gaps in research area of environmental research and analytical chemistry.

Material and Methods

Study Area: Environmental monitoring and pollution assessment study were carried out in east Antarctica during the austral summer seasons of various Indian Scientific Expeditions to Antarctica[15]. Long passage during expedition from Goa (India) to Cape Town (South Africa) and further

to east Antarctica provides an opportunity to observe and evaluate the surface seawater quality of selected sea stretch from India to Antarctica using M/V Emerald Sea.

A long stretch of Indian Ocean was selected as a sampling site for the present study. The seawater samples were collected from Goa to Cape Town (in the Indian Ocean) during the Indian Scientific Expedition to Antarctica (XXVIIth ISEA). Total eight samples were collected from Goa to Cape Town in Indian Ocean to evaluate the concentrations of selected metals. The location map of study area is given in the Indian Ocean as given in the fig. 1. Geo-coordinates of all relevant sampling points are depicted in table 1.

Sampling: The seawater sampling was carried out during the voyage at an interval of approximately 6 or 8 degree interval in the longitude. Sampling vessel, rope, sampler's hands were disinfected using IPA to avoid the contamination. The samples were collected in the clean and sterilized gamma irradiated 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 upright position maintaining the temperature 1-4°C with ice pack enclosed conditions instantly after preservation by 1 ml 70 % HNO_3.

The samples were conveyed to the laboratory using ice boxes after accomplishment of expedition and analyzed for the trace metals and major elements. Sterilized conditions were sustained during the collection of samples. The samples were retained in an ice pack to avoid any contamination of any alien material or microbial flora of the samples during the transference.

Analytical Methods: Using a cautious combination of reduction, oxidation, precipitation, extraction, chelation, filtration and concentration processes, trace metals can be accurately measured in seawater[16]. Depending upon the analyte of interest, seawater is then analysed using Hydrid 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[17]. Standards methods were followed for the dilution and analysis for various elements as described in APHA[18].

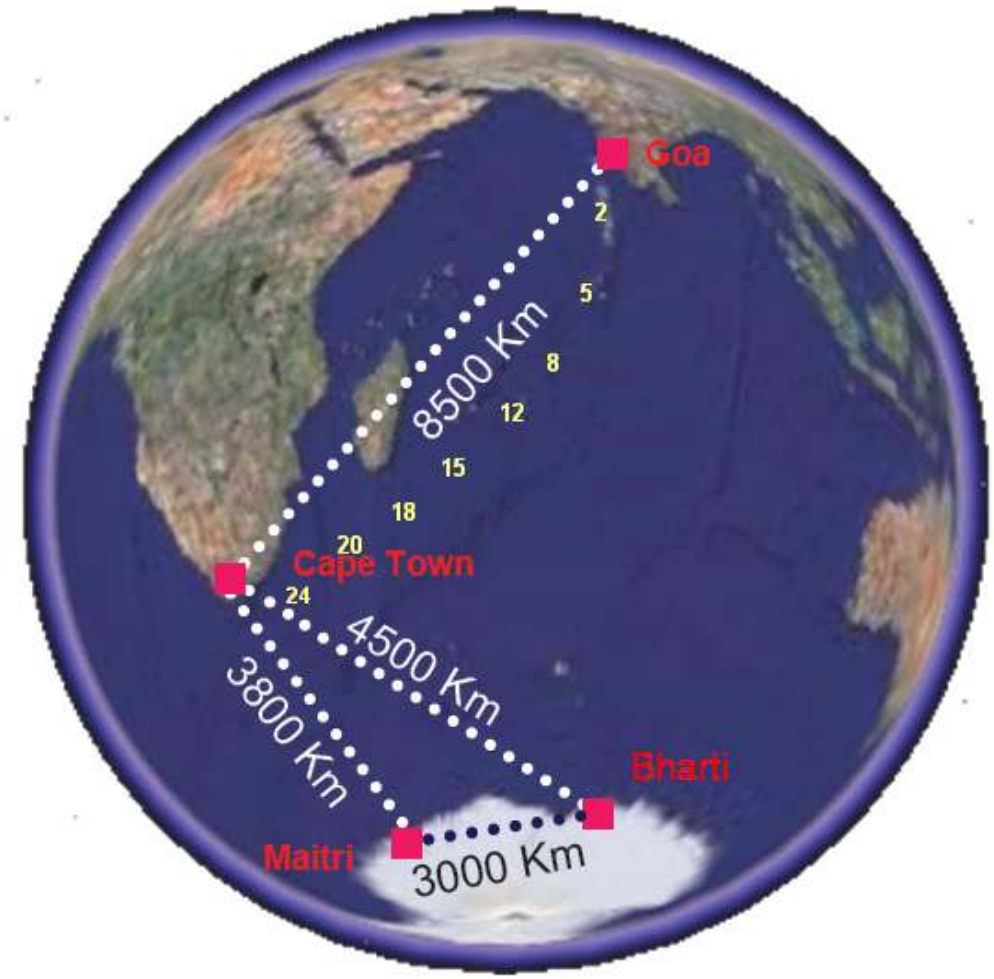

Fig. 1: Location map displaying sampling stretch in Indian Ocean (Locations cited as 2-24 are the sampling stations)

The analytical method used in this study was obtained from the modification of the one described by a group of researchers[19]. 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 every five samples, initial calibration standards and CWW-TM-D certified reference materials. 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 and a: the constant of the calibration line).

Results and Discussion

The primary examines of seawater were performed just prior to the beginning of the 19th century in laboratories. However, problems arising from changes in chemical composition through evaporation, biological activity, or chemical interactions with the containing vessel forced the marine investigator 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 quantities of materials[20].

Temperature and pH of sea water samples were recorded on spot and the values are given in table 1. Seawater temperature was recorded in a continuous decreasing order from 28.3 ºC to 21.5 ºC in Indian Ocean stretch from Goa (India) to South Africa. pH was found in fluctuating manner in entire Indian Ocean and recorded to be 8.5 to 7.9 on pH scale.

Major elements: Sodium, potassium, calcium, magnesium, boron, iron metals were found to be the dominant constituents among the major sea water contents. Maximum sodium was observed to be 99521.32 µg/cc at S-2 and minimum concentration was 40216.57 at S-20 site. Maximum concentration of potassium was found to be 4043.33 µg/cc at S-2 site and minimum was 2129.33 µg/cc at S-24 near South Africa. Maximum calcium concentration was observed to be 2411.21 µg/cc at S-5 site and minimum was 1555.9 µg/cc at S-15 site. Maximum magnesium was recorded to be 8049.49 µg/cc at S-5 site and minimum concentration was 4450.68 µg/cc at S-20 sapling point.

Maximum concentration of boron was observed to be 137.27 µg/cc at S-15 and minimum was 15.16 µg/cc at S-18 site. Maximum iron was quantified at S-20 site to be 23.35 µg/cc and minimum was 6.9 µg/cc at S-24 near Cape Town (South Africa). Beside these elements, aluminum (0.733 - 5.526 µg/cc) and zinc (0.341 - 1.574 µg/cc) were also present in significant quantities in different samples.

Table 1
On spot data of seawater samples collected from India to South Africa

S.N.	Samples Code	Latitude	Longitude	pH	Temperature (ºC)
1	S-2	N 09°22′48.2″	E 67°07′45.5″	8.5	28.3
2	S-5	N 04°56′40.7″	E 62°21′33.4″	7.9	27.7
3	S-8	N 00°10′26.8″	E 57°15′17.2″	8.0	27.7
4	S-12	S 05°51′45.6″	E 50°47′36.7″	8.1	28.5
5	S-15	S 12°50′30.8″	E 44°31′01.2″	8.1	28.2
6	S-18	S 20°05′48.5″	E 39°13′47.3″	8.2	31.2
7	S-20	S 27°40′01.3″	E 33°06′40.9″	7.9	22.6
8	S-24	S 34°54′37.7″	E 21°03′58.2″	8.1	21.5

Table 2
Quantities of major constituents in seawater samples collected from India to South Africa (µg/cc)

S.N.	Samples	Al	B	Ca	Fe	K	Mg	Na	Zn
1	S-2	1.251	45.641	1585.988	8.363	4043.330	4543.414	99521.325	0.509
2	S-5	1.850	33.391	2411.213	7.462	3215.343	8049.439	73468.950	1.004
3	S-8	1.389	17.781	2113.176	18.407	2727.730	6349.527	56593.825	1.148
4	S-12	0.979	65.908	2149.301	8.597	3022.305	7003.489	64947.325	0.804
5	S-15	4.415	137.273	1555.926	13.673	2232.480	4480.289	40771.825	0.341
6	S-18	5.526	15.163	1634.651	13.017	2769.643	6055.314	53490.075	1.574
7	S-20	4.196	19.360	1588.126	23.352	2143.293	4450.689	40216.575	0.444
8	S-24	0.733	22.778	1643.538	6.938	2129.330	4626.227	41863.075	0.380
Detection Limits		0.018	0.009	0.025	0.15	0.1	0.02	0.015	0.015

Metals: Cadmium was found in coastal regions only near Goa as well as near Cape Town (South Africa) which expresses the anthropogenic influence over cadmium introduction into sea ecosystems of both countries. Maximum cadmium concentration was observed to be 0.135 µg/cc at S-2 site near Goa (India) and 0.019 µg/cc at S-24 near Cape Town whereas it was found below detection limit in all remaining samples. Similar trend was observed for cobalt metal in seawater samples collected from coastal regions of Goa. Maximum quantity of cobalt was observed to be 0.191 µg/cc at S-2 site and 0.048 µg/cc at S-8 while it was found below detection limit in all remaining samples of sea water.

Very low concentration of chromium (0.002 µg/cc) was detected in a seawater sample at S-20 site. Selenium was also detected only in single sample at S-5 site where its value was recorded to be 0.943 µg/cc. Lead metal was present in normal quantities in two samples collected from S-8(1.176 µg/cc) and S-20 (0.336 µg/cc). Nickel was also one of the rarest metals in seawater as it was found below detection limit in all samples. Beside these elements, copper (0.095 – 0.296 µg/cc), manganese (0.037 – 0.072 µg/cc) and molybdenum (0.259 – 1.915 µg/cc) were also present in every seawater sample in trace quantities. As biological requirement, a few metals are essential for living organisms in trace quantities in ocean ecosystem. These trace metals may re-circulate from sediment to water and became available for biota[5,21].

Spatial dispersion of elements and trend from India to South Africa: In general, the total concentrations of all selected metals were present in higher ranges in coastal water and were observed to be fluctuating with the spatial variations. The observations signposted that the concentrations of metals in seashore were higher than those in inner Ocean. Metals like aluminum (0.733 –5.526 µg/cc), zinc (0.341 – 1.574 µg/cc), phosphorous (BDL – 5.796 µg/cc) and arsenic (BDL – 1.353 µg/cc) were also found in significant concentrations in almost every seawater sample. Arsenic may release into water from the earth crusts and various rocks[22]. Cadmium metal was found only in the water of seashore regions of India and South Africa in trace quantities.

Strontium was also found as one of the dominant and uniformly distributed alkaline earth metals in sea water ranging from 16.628 µg/cc to 45.69 µg/cc. However, the concentration of strontium was found to be gradually deceasing from Goa to South Africa. Arsenic and phosphorous were found maximum near Goa coastal area indicating human activities near seashores[5,23]. Some inputs may arise from the outer environment due to the anthropogenic reasons[24].

Table 3
Quantities of trace metals in seawater samples collected from India to South Africa (µg/cc)

S.N.	Samples	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	Se
1	S-2	0.135	0.191	BDL	0.203	0.053	0.378	BDL	BDL	BDL
2	S-5	0.069	BDL	BDL	0.268	0.062	0.565	BDL	BDL	0.943
3	S-8	BDL	0.048	BDL	0.117	0.050	0.349	BDL	1.176	BDL
4	S-12	BDL	BDL	BDL	0.296	0.049	0.326	BDL	BDL	BDL
5	S-15	BDL	BDL	BDL	0.244	0.037	0.259	BDL	BDL	BDL
6	S-18	BDL	BDL	BDL	0.158	0.063	0.297	BDL	BDL	BDL
7	S-20	BDL	BDL	0.002	0.192	0.072	1.915	BDL	0.336	BDL
8	S-24	0.019	BDL	BDL	0.095	0.054	0.315	BDL	BDL	BDL
Detection Limits		0.027	0.06	0.022	0.02	0.002	0.16	0.08	0.29	1.5

Table 4
Other important constituents in seawater samples collected from India to South Africa (µg/cc)

S.N.	Samples	As	Ba	P	Sr
1	S-2	1.353	0.103	1.141	45.690
2	S-5	1.281	BDL	5.796	29.708
3	S-8	BDL	0.044	BDL	23.958
4	S-12	BDL	0.056	BDL	24.944
5	S-15	BDL	BDL	BDL	17.954
6	S-18	BDL	0.065	0.974	20.289
7	S-20	BDL	0.086	BDL	16.628
8	S-24	0.485	BDL	BDL	18.451
Detection Limits		1.5	0.02	0.4	0.01

(BDL= Below Detection Limit)

Maximum concentrations of several metals like iron, magnesium, sodium, copper and strontium were recorded at sampling site S-2 and S-5 in Indian Ocean and it was because of maximum turbulence and disturbance in sea water. Nonetheless, several variables like temperature may influence over heavy metals dispersions and many traits of biogeochemical cycle of microelements in Indian Ocean[25,26].

Conclusion

Highest values of sodium and potassium were observed at S-2 site in Indian Ocean. This trend demonstrates the minutest turbulence and loading tendency of constituents in seawater and decreasing value trend towards South Africa. Temperature may also play an important role to influence and regulate this functioning in sea ecosystem. High arsenic and phosphorous quantity near Goa coast indicate human activities because some inputs may arise from the outer environment due to the anthropogenic reasons.

Strontium is one of the special constituents and the present trend can indicate the occurrence of huge natural sources of strontium in the coastal regions of India which decreases towards South Africa. Maximum concentrations of calcium, magnesium, cadmium, cobalt and strontium were recorded in Indian Ocean at sampling site S-2 and S-5. Distribution of different metals in sea stretch from India to South Africa shows different trends at coastal and Indian Ocean and not fund interrelated.

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