

Arsenic Enrichment in Estuarine Sediments – Impact of Iron and Manganese Mining

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Abstract

River Mandovi and Zuari (west coast of India) are flowing through iron and manganese mining areas and are heavily used for iron and manganese ore transport. This region generates 25-30 million tons of mining rejects per year. The iron ore of Mandovi-Zuari catchments area has approximately 50.04 $\mu\text{g/g}$ of arsenic and partial dissolution of the mining rejects could enrich the dissolved arsenic in estuaries. The seasonal variability of arsenic in water column and in the sediments was investigated in this study. During the pre-monsoon and post monsoon seasons, both estuaries had same arsenate levels (0.11-0.24 $\mu\text{g/l}$) and arsenate was low at marine end and high at freshwater end. The arsenite level was low at marine and fresh water ends with its maximum at mid estuarine region. During the monsoon months, arsenate levels had a four-fold increase (0.3-0.78 $\mu\text{g/l}$) with higher concentration in surface layer compared to the bottom layer. Arsenate was at its maximum during the period of maximum precipitation and river discharge. The high levels of arsenate indicate the possibility of some arsenic associated with iron as FeAsS leaching into river and of the dissolution of river-borne sediments. The correlation between arsenate and salinity were + 0.56, - 0.64, - 0.76 for pre-monsoon, monsoon, post monsoon seasons, respectively. The negative correlation coefficients reveal that arsenic was removed both in

freshwater and estuarine waters and that river is the main source of the metalloid. The Mn oxides significantly enhance arsenite oxidation and may be behind the high arsenate at the marine end. The co-precipitation of arsenic with Fe or adsorption onto hydrous iron oxides is also behind the low arsenate at high salinity regions. The concentrations of arsenite in both estuaries were low. In the pre-monsoon months, the arsenic exhibited an increase in sediments from marine end up to ore loading sites and a decrease in fresh water region with its range of 5.84-8.94 µg/g for Mandovi, and 5.07-10.20 µg/g for Zuari. During monsoon, the arsenic in sediments had the same trend, varying from 7.30-8.24 µg/g in Mandovi and from 6.68-8.56 µg/g in Zuari. The post monsoon arsenic in sediments was high throughout the estuaries, varying from 9.27 – 9.72 µg/g for Mandovi and from 7.97-9.22 µg/g for Zuari. It seems that iron and manganese oxides are the important components in regulating arsenic distribution in sediment. The elevated levels of iron and manganese hydroxides in sediments can explain the high arsenate concentration in the estuarine sediments.

INTRODUCTION

With an average concentration in earth crust of 1.5-2 mg/kg, arsenic ranks 20th in abundance in relation to other elements (NAS, 1977). Soil contains 4 mg/kg of arsenic with an average background level of about 7 mg/kg. In general, arsenic is so widely distributed in nature that metals prepared from sulphides ores are almost invariably arsenical. The largest sources of pollution from arsenic are agricultural chemicals such as herbicides, fungicides, rodenticides and insecticides. Most important local input of arsenic into marine environment results from smelting of non-ferrous ores and from river drainage of areas with substantial arsenic ferrous ore deposits. Leaching of exposed wastes from mining activities, accelerated erosion of land and rivers draining from large industrial areas carry increased arsenic burden from a variety of industrial and domestic sources. The arsenic concentrations in fresh waters of unpolluted areas vary, but typical values seem to be a few micrograms per liter or less. Quentin and Winkler (1974) found average value of 3 µg/l in river water and 4 µg/l in lake water in Germany. A concentration increase of 0.1% per year is reported for oceanic waters, with a net gain by oceanic water of $5.66 \times 10^4 - 13.7 \times 10^4$ tons / year (Chilvers and Peters, 1984). Marine algae contain arsenic at concentrations 2000- 5000 times greater than of the seawater. The release of arsenic resulting from the activities of man exceeded those due to natural processes (Ferguson and Gavis, 1972).

STUDY AREA

Out of the total land area of Goa (3700 sq.km), 14% land area is under mining, 25% under forest cover and 36% is used for agriculture. Rivers Mandovi and Zuari are the major rivers and are important for the economy of the territory. They flow over an area of 2500 km² that is about 68% of the total geographical area. They flow through the mining areas and are heavily used to transport iron and manganese ores to the Marmugao harbor. About two-third of the total exploitation of iron, manganese and ferromanganese ores of Goa come from the mines located in the basins and watersheds of these two rivers. In fact, 90% of iron and ferromanganese ores are transported through these estuaries in barges.

River Mandovi (Fig. 1) carries discharges from a catchments area of 1150 km², the river basin has an area of ~ 380 km² and the annual fresh water runoff has been approximated to be 16 km³, with a summer runoff ~ 0.06 km³. The river carries drainage from 435 km² of forestland. About two-third of the total mining activities in Goa are located along the Mandovi basin. There are 27 large mines that generate 1500-6000 tons of rejects/day per mine. A substantial portion of which can be expected to ultimately end up in the river.

River Zuari carries discharges from a catchments area of 550 km². The average annual freshwater run off approximated to be 9 km³, with the summer run off of about 0.03 km³ per year. Ten large mines are located in this basin generating 1000-4000 tons of rejects/day/mine. A good amount of which are added to the river.

Though considerable work has been done on different chemical aspects of the Mandovi-Zuari estuarine system, no attempt has so far been made on a systematic study on the seasonal variability and on the behavior of arsenic in the estuarine ecosystem. Such information is lacking for most of the estuaries along the Indian coast. Since the characteristic of the estuarine ecosystem is greatly influenced by the monsoon, a seasonal study seems to help to identify the behavior of arsenic during estuarine mixing.

MATERIALS AND METHODS

The Mandovi and Zuari estuarine systems are located between latitude 15°25'-15° 30'N and longitude 73° 45'E-73° 59' E (Fig. 1). In order to study the seasonal changes in arsenic, water and sediment samples were collected during every month for total arsenic analysis. Six sampling

points were identified in the Mandovi (M1 to M6) and six in the Zuari estuary (Z1 to Z6). The surface water samples were collected by clean bucket and the near-bottom samples by Niskin PVC water sampler. The sediment samples were collected with a hand operated Van Veen grab. The top 4 cm in the middle of the undisturbed sample was collected by means of a plastic spatula in order to avoid contamination from the metallic part of the grab. The sample was then transferred to acid washed and deionised water rinsed dry container and kept in ice during transport to the laboratory and stored in deep freeze until analysis could be carried out. Standard sampling and storage procedure were practiced throughout in the determination of all parameters. The arsenic and arsenate were determined in samples filtered through Millipore membrane filters applying the procedure outlined by Koroleff (1976) and detailed in Maheswari Nair (1994). The total arsenic in sediments was determined by AAS after hydride generation following the method of Andrae (1983a).

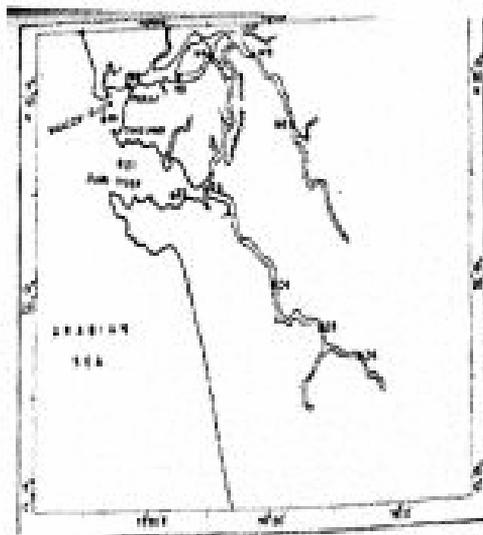


Figure 1: Sampling stations in Mandovi and Zuari rivers

RESULTS AND DISCUSSION

Arsenate Distribution

Information on the behavior of arsenic for Indian estuarine waters is at present limited. The dominant form of arsenic in both saline and fresh water regions is the inorganic arsenic i.e., arsenate. In the estuarine waters of the Mandovi and Zuari, arsenate was found to be the dominant

species. Fondekar and Reddy (1974) had reported arsenic concentration of up to $0.57 \mu\text{mol/l}$ in Zuari estuary. Similar concentrations were also reported by Zingde et al. (1976) in the estuaries and coastal waters around Goa. In the pre-monsoon months, the arsenate concentration in the surface waters of Mandovi estuary varied from 0.011 to $0.22 \mu\text{g/l}$ with 0.13 to $0.27 \mu\text{g/l}$ in the bottom layer. For the Zuari estuary, it varied from 0.13 to $0.20 \mu\text{g/l}$ in the surface layer and 0.18 to $0.24 \mu\text{g/l}$ for the bottom layer. At few stations, the bottom arsenate levels were found to be higher than of the surface values. It was also noticed that the concentration of arsenate and dissolved oxygen followed the same pattern of low at the marine end and high at the fresh water end. But in the case of arsenite, it was the reverse, with low values in the marine as well as in the freshwater zone, with a maximum in the mid – estuarine region. One of the factors that may be responsible for the high arsenate to arsenite ratio in the waters might be the differential reaction characteristic for co-precipitation of these forms with iron oxide (La peintre, 1954).

During the pre-monsoon, the bottom values of arsenate (Fig. 2) were high at Z1 to Z3 with a minimum at Z5, while the surface values had its maximum only at Z3. All other stations had a low constant value throughout. In Mandovi, the bottom concentrations decreased from M6 to M5. In the mid-estuary, the concentrations were very low with another high concentration at M2. The reason for an increase of arsenate at M2 after the minimum at M3 during the monsoon could possibly be due to a possible reducing condition prevailing at the sediment water interface, caused by stratification resulting in poor vertical exchange resulting from the presence of a salt wedge. In the salt wedge region, the bottom water and the sediment can become oxygen depleted due to organic matter decomposition. Metals like arsenic are released into the overlying waters due to the low redox potential. This may also be a reason for high values of arsenic during the monsoon months.

During the monsoon season, the arsenate had the highest levels as compared to other seasons of the year (Fig. 2). The surface values ranged from 0.40 to $0.78 \mu\text{g/l}$ and from 0.34 to $0.79 \mu\text{g/l}$ for the bottom waters of the Mandovi estuary. For Zuari estuary, it ranged from 0.45 to $0.79 \mu\text{g/l}$ at the surface and from 0.42 to $0.78 \mu\text{g/l}$ at the bottom. The surface values were higher than the bottom values in both the estuaries. The bottom values were higher at the mouth of the estuary, but the concentration of arsenate was the highest in the upstream, appeared to be the effect of land drainage. The large variations observed at various stations reflected its chemical instability and much of it appeared to be lost to the sediments by way of precipitation and adsorption. This was evident from the relatively high values found at the bottom layers. The

other evidence for this could be inferred from the relatively low values at the marine end as compared to the higher concentration at the fresh water region. The higher concentrations of arsenate in the estuaries in the monsoon months as compared to other seasons confirmed the land origin of the arsenate. Higher concentration in the bottom layer suggests active recycling of the element. The disturbances of bottom sediment in the monsoon months could be another reason for the high concentration in the water column in both the estuaries. During the monsoon months, the sediments are re-suspended leading to a release of arsenic into the water column. The drainage from the iron and manganese ore mines to the upper reaches of the estuary coupled with the high and frequently mixed turbidity conditions of the estuary during the monsoon period might explain the variations in arsenate levels in the estuaries. The concentrations of arsenic in two iron ore samples analyzed were 50.44 $\mu\text{g/g}$ and 48.93 $\mu\text{g/g}$, respectively and hence a partial dissolution of the mining rejects could lead to high concentration of dissolved arsenic in the riverine region. Hence the high concentration of arsenate at M6 and Z6 could be due to the hydrous oxide precipitates from the weathering zone brought by the river-end from the nearby mine areas. The effect of this seemed to be decreasing in the seaward direction. About 70% of the iron is mined from north Goa and is loaded between M5 and M6 and the remaining 30% from South Goa near station Z5 and Z6, where high concentrations of arsenate were reported.

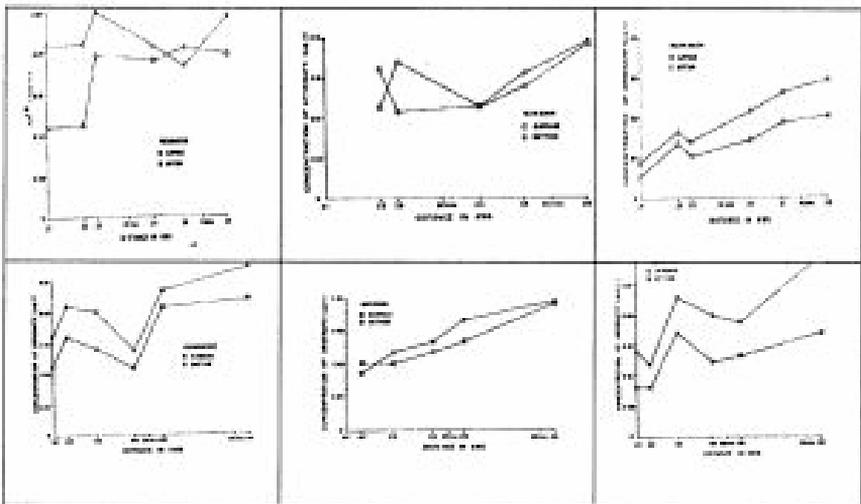


Figure 2: Seasonal variation of arsenate in Zurai and Mandovi rivers

The high concentration of arsenate may be the result of a re-mobilization processes that transfer arsenic to the water column from suspended matter or from deposited sediments. Such mechanisms have been identified in some estuaries such as the Puget Sound, Tamar and involve arsenic diffusion from pore waters or desorption from suspended matter (Carpenter et al., 1978, Howard et al, 1984). In the present estuarine region with salinity $15-30 \times 10^{-3}$, the arsenate levels were remarkably stable. Near the marine end, where arsenate levels of less than $0.05 \mu\text{g/l}$ are to be anticipated, the presence of elevated levels could be explained only by a significant input in this region. Release from river-born sediments is an additional source of arsenic.

During the post monsoon months, the arsenate varied (Fig.2) from 0.08 to $0.17 \mu\text{g/l}$ in the surface waters and from 0.12 to $0.30 \mu\text{g/l}$ in the bottom waters of Mandovi estuary. In Zuari estuary, the ranges were $0.05-0.020 \mu\text{g/l}$ for surface layer and 0.09 to $0.29 \mu\text{g/l}$ for the bottom waters. The concentrations were higher in bottom waters than the surface layer in Mandovi estuary. While in Zuari, at Z1 the surface value was higher than the bottom waters, where after a steady decrease took place. Once again, the bottom values were higher from stations Z2 to Z6.

The post monsoon values were more or less similar to the pre-monsoon values. Even though there was a variable but steady increase towards the upper reaches, both the surface and bottom values at station Z2 showed a maximum in Zuari, while a maximum was observed at M3 in Mandovi, during the same period. These types of sudden changes may be due the dynamic nature of the estuaries or even due to the influence of certain local disturbances such as plankton or benthic production or due to the presence of sewage outlets. The Panjim city sewage outlet joins the river Mandovi somewhere before station M2. The sewage from the Mandovi showed an arsenate concentration of $0.23 \mu\text{g/l}$ and $0.08 \mu\text{g/l}$ of arsenite. The sewages collected from Zuari had $0.08 \mu\text{g/l}$ of arsenate and $0.03 \mu\text{g/l}$ of arsenite. This could explain the high values of arsenate in Mandovi and the relative role of sewage pollution in enriching the estuary with arsenic.

Arsenite Distribution

Significant amounts of arsenite were present in both the estuarine waters. It was observed that arsenite exhibited a maximum at stations where arsenate was low in concentration and vice versa. The presence of arsenite in the estuaries indicates the existence of simultaneous activity of bacteria that can reduce arsenate to arsenite. Johnson (1972) reported the evidence of microbial reduction of arsenate to arsenite.

During the pre-monsoon months, the arsenite levels were very low in the surface and bottom waters. Average values of arsenite during the three seasons are given in Table 1. The arsenate concentration varied from undetectable levels to 0.07 $\mu\text{g/l}$ for surface waters, and from undetectable values to 0.10 $\mu\text{g/l}$ in the bottom waters of Mandovi. For the Zuari waters, it varied from 0.04 to 0.11 $\mu\text{g/l}$ and 0.07 to 0.10 $\mu\text{g/l}$ for surface and bottom waters, respectively. Surface and bottom waters in Mandovi did not show any significant variation at most of the stations except at M2 and M6. The arsenite levels showed two small peaks, one at M2 near the mouth of the estuary and one at M6. There was a drop at M5 both at the surface and in the bottom waters. In Zuari too, a peak was noticed at estuary mouth Z2 with a drop in surface arsenite level at Z3 and with an elevated bottom concentration. Both surface and bottom concentrations were low at Z6. In unpolluted natural waters, the occurrence of arsenite seems to be closely linked to primary productivity. During high biological productivity periods arsenate is taken up readily by planktonic algae whereas arsenite is released in the surrounding media (Andreae, 1978). Hence the high values of arsenite at the mouth of estuary seemed to be controlled by phytoplankton population. Diatoms generally dominated the phytoplankton population.

Table 1: Average values of arsenite ($\mu\text{g/l}$) in Madovi estuary. The entries in brackets are for Zuari estuary

Surface	Pre-Monsoon	Monsoon	Post-Monsoon
M1 (Z1)	0.05 (0.07)	0.08 (0.18)	0.04 (0.02)
M2 (Z2)	0.04 (0.11)	0.09 (0.17)	0.07 (0.04)
M3 (Z3)	0.07 (0.09)	0.07 (0.16)	0.15 (0.04)
M4 (Z4)	0.06 (0.10)	0.17 (0.06)	0.06 (0.06)
M5 (Z5)	0.00 (0.05)	0.12 (0.19)	0.09 (0.05)
M6 (Z6)	0.05 (0.04)	0.14 (0.15)	0.07 (0.14)
Bottom			
M1 (Z1)	0.03 (0.07)	0.07 (0.18)	0.05 (0.03)
M2 (Z2)	0.10 (0.16)	0.07 (0.16)	0.09 (0.04)
M3 (Z3)	0.07 (0.09)	0.13 (0.11)	0.18 (0.07)
M4 (Z4)	0.07 (0.07)	0.06 (0.09)	0.11 (0.09)
M5 (Z5)	0.00 (0.13)	0.08 (0.14)	0.10 (0.07)
M6 (Z6)	0.07 (0.08)	0.12 (0.13)	0.09 (0.04)

There was no trend of variation for the arsenite levels during the monsoon months. The levels varied from 0.07 to 0.17 $\mu\text{g/l}$ and 0.06 to 0.13 $\mu\text{g/l}$, respectively for surface and bottom waters of Mandovi, with

corresponding values of 0.06 – 0.19 and 0.09 – 0.16 $\mu\text{g/l}$ for the Zuari estuary.

During the post monsoon months, arsenite was found only in very low concentrations. It varied from 0.04-0.15 and 0.05-0.18 $\mu\text{g/l}$ in surface and bottom waters, respectively in Mandovi with corresponding values of 0.02-0.06 and 0.03-0.09 $\mu\text{g/l}$ for Zuari waters. Arsenite exhibited a mid estuarine peak in both the estuaries. The river runoff was higher compared to pre-monsoon months, but the arsenite levels were not as high as in the pre-monsoon. The pre-monsoon season had the highest arsenite levels while monsoon period had the least. The arsenite concentration during the post-monsoon had nearly coincided with its values during the pre-monsoon. The river discharge seemed to be the main factor behind the seasonal variability of arsenite in both the estuaries.

Arsenic in Estuarine Sediments

The estuarine sediments are sinks for many materials transported from land. The arsenic in soils is typically 0.1 – 4.0 mg/kg but can be greatly elevated in mineralized areas. The levels of it in freshwater lake sediments might be expected to reflect the naturally occurring arsenic content of the soils of the corresponding catchments areas, except for regions with a significant input of it from industries and agriculture. Analysis of soil from the Mandovi-Zuari catchment areas had shown an elevated arsenic level of order of 9.48 $\mu\text{g/g}$ (dry wt) in soil sample from the mining areas of Mandovi, while in the samples slightly away from the mining areas arsenic concentrations varied from 5.58-7.93 $\mu\text{g/mg}$ (dry wt). This explains the occurrence of high level of arsenic towards the upstream stations of both estuaries.

During the pre-monsoon months, the sedimentary arsenic had shown an increase from the marine end till M5 and with a decrease towards the fresh water region. The maximum level was observed more upstream. The concentration ranged from 5.84 to 8.94 $\mu\text{g/g}$ (dry wt) for the Mandovi; while in Zuari it ranged from 5.07-10.20 $\mu\text{g/g}$ during the pre monsoon season. The values were high both at the marine and fresh water ends, with low levels at the mid regions. The minimum concentration was at M4 and the maximum was at M6. During the monsoon months, both the estuaries had the same trend with high values at the marine end, with maximum at stations M5 and Z4 and with an increasing trend towards the fresh water end. The values ranged from 7.30 – 8.24 $\mu\text{g/g}$ in Mandovi and 6.68 to 8.56 $\mu\text{g/g}$ for Zuari. During the post monsoon, the concentration was higher throughout the estuary. The trend was same for Zuari also.

The values ranged from 9.27 to 9.72 $\mu\text{g/g}$ (dry wt) for sediments of Mandovi; while for Zuari it ranged from 7.97 to 9.22 $\mu\text{g/g}$ (dry wt).

The fixation of arsenic in marine mud takes place largely as a result of their ferric hydroxide content. Peterson and Carpenter (1986) have suggested that both iron and manganese oxides are important components regulating arsenic distribution in coastal sediments. In the Mandovi and Zuari estuarine sediments high concentration of iron and manganese hydroxide were reported at the freshwater end (Jayakumar, 1987). Hence the high concentration of arsenic at the fresh water end could be due to the above reasons. The effect of this can be seen decreasing seawards in the Mandovi, while the trend was the reverse in the Zuari.

CONCLUSIONS

The correlation between arsenate and salinity was +0.56, -0.64 and -0.74 for pre-monsoon, monsoon and post monsoon seasons, respectively. The negative correlation revealed an arsenic removal both in the freshwater and estuarine waters and indicated the river as the source of the metalloid. Arsenic removal was observed in 81% of samples collected during the monsoon and 90% of samples collected during the post monsoon. During the post monsoon, there was a clear sign of addition of arsenite. At the high saline region, however, addition had decreased and this was evident in Zuari estuary

REFERENCES

- Andreae, M.O. (1978), Distribution and speciation of arsenic in natural waters and some marine algae. *Deep Sea research*, 25, 391 – 402.
- Andreae, M.O. (1983a), Arsenic (by Hydride generation /AAS). In: *Methods of seawater analysis*, 2nd Edition (Grasshoff K., Erhardt, M., Kremling, K. eds.), Weinheim: verlag Chemie, 218 –225.
- Carpenter , R., Peterson, M.L. and Jannke, R.A. (1978), Sources sinks and cycling of arsenic in the Puget Sound region. In: M.L.Wiley (Editor). *Estuarine Interaction*, Academic press, New York, 459 – 480.
- Chilvers, D.C. and Peterson, P.J. (1984), Global cycling of arsenic. In: Paper presented for Scientific Committee for problems of the environment (SCOPE) Workshop on metal cycling in the environment. Toronto, Canada, 3-6 September.

- Ferguson, J.P. and Gavis, J. (1972), A review of the arsenic cycle in natural waters. *Water Research*, 6, 1259 – 1274.
- Fondekar, S.P. and Reddy, C.V.G. (1974), Arsenic contents in the coastal and estuarine waters around Goa. *Mahasagar- bull.nat.Inst. Oceanogr.*, 7, 27-32.
- Howard, A.G., Arab-Zavar, N.H. and Apte, S. (1984), The behaviour of dissolved arsenic in the estuary of river Beaulieu. *Estuar. Coast. Shelf Sciences*, 19, 493 –504.
- Johnson, D.L. and Pilson, M.E.Q. (1972), Arsenate in the western north Atlantic and adjacent regions. *Journal of Marine Research*, 30, 140-149.
- Jayakumar, D.A. (1987), Seasonal distribution of organic matter in mangrove. *Indian Journal of Marine Sciences*, 16, 103 –106.
- Koroleff, F. (1976), Determination of arsenic. In: *Methods of sea water analysis*, Verlag Chemie. p 158 –166.
- La peintre, M. (1954), Solubilization par les eaux naturelles de l'arsenic lie au fer dans les roches sedimentaries. *C.R. Acad. Sciences.*, 239, 359-360.
- Maheswari N. (1994), Study of arsenic and related parameters along the central west coast of India. Ph.d thesis , Goa university, India, pp 209.
- NAS (1977), medical and biological effects of environmental pollutants: Arsenic. National Academy of Sciences., Washington.
- Peterson, M.L. and Carpenter, R. (1986), Arsenic distribution in pore waters and sediments of Puget Sound, lake Washington, the Washington coast and Saanich inlet, B.C. *geochemica et Cosmochemica Acta.*, 50, 353-369.
- Quentin, K.W. and Winkler, H.A. (1974), Occurrence and determination of inorganic polluting agents. *Zentralblatt Bakteriologie (Orig.B)*, 158:514-523.
- Zingde, M.D., Singbal, S.Y.S, Moraes, C.P. and Reddy, C.V.G. (1976), Arsenic, Cu, Zn and Mn in the marine flora and fauna of coastal and estuarine waters around Goa. *Indian Journal of Marine Sciences*, 5, 212-217.