

# ARSENATE AND ARSENITE LEVELS IN THE COASTAL AND ESTUARINE WATERS OF GOA

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## ABSTRACT

Arsenate and arsenite concentrations were determined in estuarine and coastal waters around Goa during the pre-monsoon months (February to April). Arsenate was found to be the dominant form in both the systems. In the estuarine waters, arsenate varied from  $< 1 \mu\text{g/l}$  to  $21.75 \mu\text{g/l}$  (av.  $5.28 \mu\text{g/l}$ ) and arsenite from  $< 1 \mu\text{g/l}$  to  $18.75 \mu\text{g/l}$  (av.  $2.54 \mu\text{g/l}$ ) while in coastal waters, it ranged from  $< 1 \mu\text{g/l}$  to  $24.0 \mu\text{g/l}$  (av.  $5.91 \mu\text{g/l}$ ) and arsenite from  $< 1 \mu\text{g/l}$  to  $9.0 \mu\text{g/l}$  (av.  $1.43 \mu\text{g/l}$ ). A few estimations of the total arsenic in the estuarine and coastal sediments indicate marked accumulation of this element (4 - 14 ppm). The observed variations in the waters are attributed to the differential intensities of chemical and biological oxidation in the system, microbial reduction and the mixing processes.

## INTRODUCTION

Arsenic is one of the elements in sea water currently under investigation in view of its reported toxicity to marine animals and human beings. It is interesting to note that toxicity of arsenic increases greatly when arsenic is reduced from + 5 to + 3 oxidation state. To humans, arsenate is about 60 times less toxic than arsenite (Webb, 1966).

The present study refers to relative concentrations of soluble inorganic forms of arsenic which is an extension of the earlier work by the authors on the total soluble inorganic arsenic in the coastal and estuarine waters around Goa (Fondekar and Reddy, 1974). A few observations on total arsenic content of the inshore and estuarine sediments are also included.

## METHODS

Arsenate and arsenite in the water samples were estimated by the method described by Johnson and Pilson (1972). Total arsenic in the mud samples was determined after oxidation with nitric acid (Sandell, 1959) and using the technique of Vasak and Sedivec (1952).

Four stations were worked in both Mandovi and Zuari estuaries and four in the inshore region as shown in Fig. 1. The period of collection extended from February 1975 to April 1975. Water samples from the surface were collected using a clean plastic bucket and from the bottom, using a Van Dorn Sampler. Sediment samples were collected by means of Van Veen Grab.

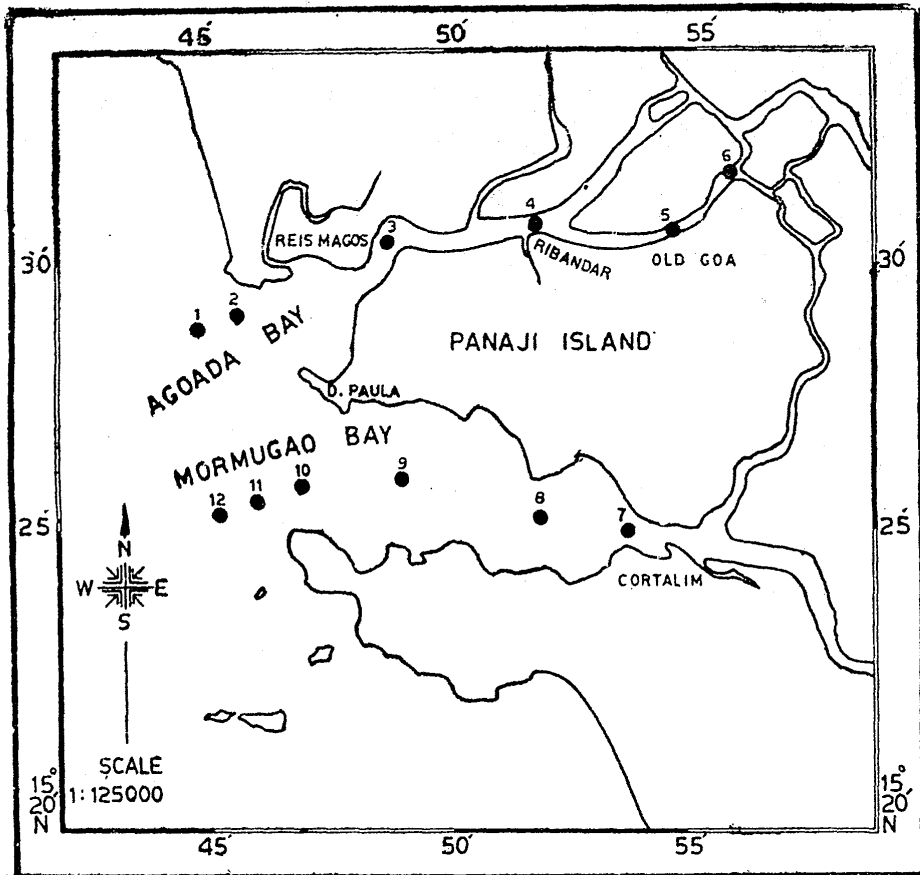


Fig. 1 — Map showing the station locations.

#### RESULTS AND DISCUSSION

Tables I and II give the concentrations of arsenate and arsenite in the two estuaries and also in the inshore region. Total arsenic content in the sediments is given in Table III. It can be seen that the average concentration of the total soluble inorganic arsenic in the Mandovi estuary is higher than that of Zuari estuary. This is because that the iron ores are always enriched with arsenic owing to the high adsorptive capacity of the hydrous iron oxides (Shnyukov, 1963). In Goa, large

quantities of iron ore are mined and shipped more through Mandovi estuary than from Zuari estuary. The arsenic content in the inshore region varied from  $< 1 \mu\text{g/l}$  to  $26.25 \mu\text{g/l}$  which was higher than the normal reported value of  $3 \mu\text{g/l}$  for sea water (Wedepohl, 1969). The high arsenic concentrations might be the overall effect of the land drainage contributing to significant accumulation of the element in the waters and sediments. During monsoon, high surface concentrations were reported in the estuaries (Fondekar and Reddy, 1974).

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TABLE I — Arsenate and arsenite concentrations in Mandovi and Zuari estuaries

Station Nos.	Depth (m)	Month	AsO <sub>3</sub> <sup>3-</sup> -As (µg/l)		AsO <sub>4</sub> <sup>3-</sup> -As (µg/l)		Total inorg. As (µg/l)		Arsenate/ Total inorg. As (%)	
			S	B.	S	B	S	B	S	B
3 <i>Mandovi estuary</i>	9	Feb.	N.D.	N.D.	N.D.	3.75	-	3.75	-	100
		Mar.	N.D.	N.D.	15.75	16.50	15.75	16.50	100	100
		Apr.	N.D.	4.50	3.75	1.50	3.75	6.0	100	25
4	5	Feb.	1.50	1.50	1.50	1.50	3.0	3.0	50	50
		Mar.	5.25	18.75	12.75	1.50	18.0	20.25	71	7
		Apr.	1.50	8.25	6.75	2.25	8.25	10.50	82	21
5	5	Feb.	N.D.	N.D.	N.D.	N.D.	-	-	-	-
		Mar.	N.D.	N.D.	18.0	21.75	18.0	21.75	100	100
		Apr.	N.D.	N.D.	1.50	N.D.	1.50	-	100	-
6	3	Feb.	N.D.	N.D.	2.25	N.D.	2.25	-	100	-
		Mar.	3.75	7.50	18.0	13.50	21.75	21.0	83	64
		Apr.	2.25	4.50	6.75	4.50	9.0	9.0	75	50
7 <i>Zuari estuary</i>	3	Feb.	N.D.	N.D.	N.D.	N.D.	-	-	-	-
		Mar.	3.0	2.25	5.25	4.50	8.25	6.75	63	68
		Apr.	N.D.	N.D.	N.D.	4.50	-	4.50	-	100
8	8	Feb.	N.D.	N.D.	N.D.	N.D.	-	-	-	-
		Mar.	9.75	17.25	3.75	3.75	13.50	21.0	28	18
		Apr.	N.D.	N.D.	N.D.	5.25	-	5.25	-	100
9	6	Feb.	N.D.	N.D.	N.D.	4.50	-	4.50	-	100
		Mar.	9.75	N.D.	N.D.	4.50	9.75	4.50	0	100
		Apr.	15.0	N.D.	7.50	9.75	22.50	9.75	33	100
10	11	Feb.	N.D.	N.D.	N.D.	3.75	-	3.75	-	100
		Mar.	6.0	N.D.	18.0	3.75	24.0	3.75	75	100
		Apr.	N.D.	N.D.	4.50	16.50	4.50	16.50	100	100

S - Surface

B - Bottom

N.D. - Not Detectable (< 1µg/l)

TABLE II — Arsenate and arsenite concentrations in the inshore region

Sta. No.	Depth (m)	Month	AsO <sub>3</sub> <sup>3-</sup> -As (µg/l)			AsO <sub>4</sub> <sup>3-</sup> -As (µg/l)			Total inorg. As (µg/l)			Arsenate/Total inorg. As (%)		
			S	MD	B	S	MD	B	S	MD	B	S	MD	B
1	20	Feb.	N.D.	6.0	N.D.	11.25	N.D.	N.D.	11.25	6.0	-	100	0	-
		Mar.	2.25	4.50	3.0	16.50	N.D.	17.25	18.75	4.50	20.25	98	0	85
		Apr.	N.D.	N.D.	N.D.	3.0	5.25	N.D.	3.0	5.25	-	100	100	-
2	10	Feb.	N.D.	-	N.D.	N.D.	-	N.D.	-	-	-	-	-	-
		Mar.	N.D.	2.25	N.D.	9.0	24.0	15.75	9.0	26.25	15.75	100	91	100
		Apr.	3.0	5.25	N.D.	4.50	N.D.	N.D.	7.50	5.25	-	60	0	-
11	10	Feb.	N.D.	N.D.	N.D.	3.75	3.75	4.50	3.75	3.75	4.50	100	100	100
		Mar.	9.0	N.D.	N.D.	3.0	10.50	15.0	12.0	10.50	15.0	25	100	100
		Apr.	1.50	1.50	N.D.	7.50	4.50	3.75	9.0	6.0	3.75	83	75	100
12	20	Feb.	N.D.	N.D.	N.D.	N.D.	4.50	6.0	-	4.50	6.0	-	100	100
		Mar.	N.D.	7.50	6.0	7.50	3.0	8.25	7.50	10.50	14.25	100	28	58
		Apr.	N.D.	N.D.	N.D.	9.0	6.75	5.25	9.0	6.75	5.25	100	100	100

S - Surface  
 B - Bottom  
 MD - Mid Depth  
 N.D. - Not Detectable (< 1µg/l)

TABLE III—Total arsenic in the marine and estuarine sediments

	Station Nos.	Depth (m)	Arsenic (ppm)
<i>Inshore region</i>	1	20	11
	2	10	10
	11	10	11
	12	20	13
<i>Mandoyi estuary</i>	3	9	9
	4	5	6
	5	5	4
	6	3	9
<i>Zuari estuary</i>	7	3	10
	8	8	14
	9	6	7
	10	11	10

The major inorganic forms of arsenic in aquatic systems are arsenate ( $\text{As}^{+5}$ ) and arsenite ( $\text{As}^{+3}$ ). In the inshore and estuarine waters of Goa, arsenate was found to be dominant (50 to 100% of the total). This is consistent with the thermodynamic considerations that arsenate is the more stable form (Sillen, 1961). Arsenite was found to be in very low concentrations. Arsenate content in the estuaries during the pre-monsoon period varied from  $< 1 \mu\text{g/l}$  to  $21.75 \mu\text{g/l}$  with an average of  $5.28 \mu\text{g/l}$ , while that of arsenite varied from  $< 1 \mu\text{g/l}$  to  $18.75 \mu\text{g/l}$  with an average of  $2.54 \mu\text{g/l}$ . In the inshore region, arsenate varies between  $< 1 \mu\text{g/l}$  to  $24.0 \mu\text{g/l}$  with an average of  $5.91 \mu\text{g/l}$  and arsenite from  $< 1 \mu\text{g/l}$  to  $9.0 \mu\text{g/l}$  with an average of  $1.43 \mu\text{g/l}$ . Generally in the estuaries, the bottom values of arsenate and arsenite are higher than in the surface waters and in the case of

inshore region the waters at the surface and mid-depths show relatively higher levels. Thus it could be seen that concentration variations in particular chemical form are also found to be very wide in both the estuarine and the coastal systems. The relative concentrations of arsenate and arsenite in the waters, appear to be controlled by the redox potential and the activity of the organisms in both water and sediments. It is suggested that organisms may catalyse the oxidation of arsenite to arsenate (Ferguson and Gavis, 1972). Higher concentrations of arsenate over arsenite is in conformity with the well oxygenated conditions of the waters (higher redox potential) coupled with perhaps, the catalytic activity of the oxidising organisms. The presence of significant amounts of arsenite in the water column at random also suggests the existence of simultaneous activity of

bacteria which can reduce arsenate to arsenite. Johnson (1972) reported the evidence of microbial reduction of arsenate to arsenite. Diverse biological transformations of arsenic to different forms render it difficult to assess the nature of contribution for the dominance of any particular chemical form of the arsenic, particularly in well oxygenated waters. Nevertheless, the observed variations of total arsenic concentrations and the relative levels of arsenate and arsenite indicate that organisms may also partly play a dynamic role in controlling the standing levels of arsenic in its different chemical forms (Ferguson and Gavis, 1972). The other factor which may also be responsible for the high arsenate to arsenite ratio in the waters might be the differential reaction characteristics for co-precipitation of these forms with iron oxide (La Peintre, 1954; Gupta and Ghosh, 1953).

An interesting feature that could be noticed is that the concentrations of arsenic in the waters of Mandovi are higher than in Zuari, whereas in the case of sediments, the conditions are reversed. Inshore sediments show higher arsenic concentrations and in the waters the concentrations are in between those of estuaries. These observations indicate that the recycling and dispersion characteristics are diverse depending on the biogeochemical nature of the sediments and the intensities of stratification

in the water column. In Zuari estuary, the concentration of arsenic in the sediments is high and the extent of regeneration which is also marked as indicated by significant arsenite content of the waters at random, suggests that restricted dispersion may be responsible for low arsenic in the waters as compared with Mandovi estuary and the inshore region.

Another significant observation is that, in the months of March and April, there is a marked increase in the arsenic concentration, in both coastal and estuarine waters. Arsenate to arsenite ratio also attains maximum at most of the stations. Unlike in the monsoon, land drainage in the pre-monsoon period is insignificant to account for the sharp increase in the values and this leaves the only possibility that the regeneration of arsenic forms is very active in the estuarine and coastal systems. The regeneration might be due to chemical or biological oxidation or because of microbial reduction. Higher arsenate over arsenite concentrations of the water tend to suggest the dominance of chemical or biological oxidation over that of microbial reduction during this period.

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