

ARSENIC CONTENT IN THE COASTAL AND ESTUARINE WATERS AROUND GOA

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ABSTRACT

Soluble inorganic arsenic concentrations in the coastal and estuarine waters of Goa, showed marked variations with location. The concentrations in the inshore region varied from $< 1 \mu\text{g/l}$ to $43 \mu\text{g/l}$, and in the estuarine waters (Zuari) from $3 \mu\text{g/l}$ to $67 \mu\text{g/l}$. The values in the inshore waters were relatively higher than those normally reported for sea water. Much of the arsenic in the coastal waters seems to be of land origin as evidenced by higher concentrations in the estuaries especially during the monsoon period. The observed large variations at different locations reflect on its chemical instability and much of it appears to be lost to the sediments by way of precipitation and adsorption.

INTRODUCTION

Arsenic is one of the toxic trace metals present in the sea and very little is known about its distribution. Fishes and other marine organisms are known to concentrate the element in significant proportions from the environment. This being a cumulative poison, it may prove hazardous to human beings in the event of consuming the marine animals having high concentrations of arsenic in their tissues. Since the concentration levels in the organisms mostly depend on the concentration of the medium, it is essential to have a knowledge on the distribution of arsenic in the sea, and the surrounding water systems. Only recently some concern is evinced regarding the distribution of this element in the sea-water (Rakestraw and Lutz, 1933; Armstrong and Harvey, 1951; Smales and Pate, 1952; Portmann

and Riley, 1964). Practically no information is available in the Indian waters. As a first step to understand the cycle of arsenic in the marine environment, some observations were made in the coastal and estuarine waters of Goa (central west coast of India). The present paper gives a preliminary account on the distribution of soluble inorganic arsenic.

METHODS

Surface samples were collected using clean plastic bucket and the bottom samples using a Van Dorn Sampler. Samples were analysed for soluble inorganic arsenic (arsenate + arsenite) using the phosphate method of Murphy and Riley (1962) as modified by Johnson (1971) and Johnson and Pilson (1972). An aliquot of the sample is oxidised with potassium iodate to convert arsenite to arsenate which on treatment with mixed reagent develops

molybdenum blue colour. The extinction of the molybdenum blue is proportional to $\text{PO}_4^{3-}\text{-P}$, $\text{AsO}_4^{3-}\text{-As}$ and $\text{AsO}_3^{3-}\text{-As}$ concentrations. Another aliquot is reduced with acidified sodium metabisulphite and sodium thiosulphate solutions converting the arsenate to arsenite and the extinction of the developed molybdenum blue, which is due to $\text{PO}_4^{3-}\text{-P}$, alone is measured. The difference between the oxidised and reduced extinctions is due to $\text{AsO}_4^{3-}\text{-As}$, and $\text{AsO}_3^{3-}\text{-As}$, which is considered as soluble inorganic arsenic. Standard arsenic solutions are prepared using reagent grade arsenic trioxide. Extinctions are measured in SP 500 UNICAM Spectrophotometer at 865 m μ using 10 cm cells.

Pernem (4 stations), (ii) off Aguada (4 stations) (iii) off Mormugao (3 stations), and (iv) off Colva (2 stations) were selected as shown in Fig. 1. Moreover, four stations 9, 10, 11 and 12 were covered in the Zuari estuary. Three stations, 16, 17 and 18 were particularly occupied between Mormugao and Colva, near Velsao area, wherein the fertilizer factory Zuari Agro-Chemicals Limited, is situated. The factory uses arsenic trioxide in the process for manufacturing urea and discharges its effluent directly into the sea. Present observations, relate to the period March to May in the year 1973. Few observations were also made in the estuarine waters during the monsoon period.

Four perpendicular sections (i) off

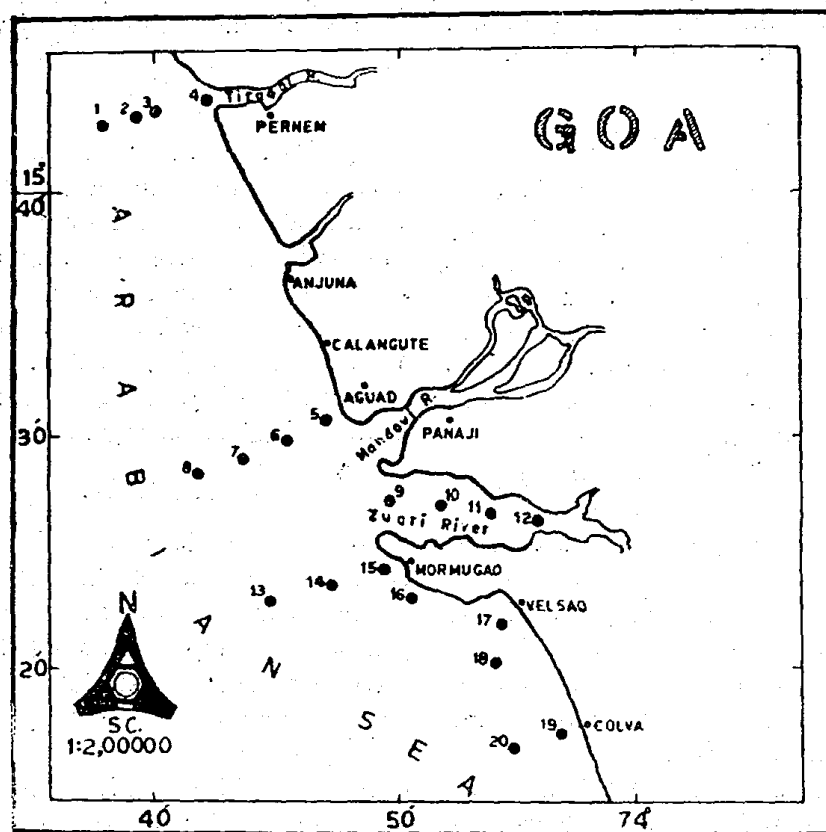


Fig. 1 Map showing the station locations.

RESULTS AND DISCUSSION

Table I summarises the results obtained. Arsenic concentrations in the coastal and estuarine waters showed wide variations. In general, the concentrations in the inshore region varied from $< 1 \mu\text{g/l}$ to $43 \mu\text{g/l}$ and in the estuarine waters (Zuari) from $3 \mu\text{g/l}$ to $67 \mu\text{g/l}$. High concentrations were normally found in the bottom waters of the inshore region, whereas in the estuarine waters, surface concentrations were high at stations upstream (11 and 12) and reverse was the case at stations (9 and 10) near the mouth. In most cases, the concentrations in the coastal waters were found to be considerably higher (3 to 20 times) than those normally found in sea water. It is interesting to note that the arsenic content of waters off Aguada and Mormugao were not detectable ($< 1 \mu\text{g/l}$) in both the surface and bottom layers, whereas, significant concentrations were found north and south of these sections, specially in the bottom waters, very near to the coast. At the three stations 16, 17 and 18, between Mormugao and Colva, the surface values were quite normal, while the bottom values were high and variable. These observations proved to be useful later on, during the period September to November 1973, when a few observations made in this region, showed very high concentrations ($16 \mu\text{g/l}$ to $583 \mu\text{g/l}$). These indicated a marked influence of the effluent discharge from the fertilizer factory which was in full operation during that period. However, this effect was not felt in other regions away from the Velsao area.

Arsenic does not occur alone in nature. It occurs mainly as arsenides of

the trace metals and as orpiment and is usually associated with ores of copper, zinc, lead and tin (Halstead, 1973). It also occurs in association with iron as arsenical pyrites (FeAsS). In view of the rapid growth of industrialization and application of modern methods of agricultural farming, considerable amounts of arsenical compounds are in use which find their way into the coastal waters through rivers as land discharge or come directly through the industrial effluents. Very little is known about the arsenic cycle in marine ecosystems. Its apparent chemical resemblance with phosphorus suggests that arsenic may also occur as soluble and insoluble organic and inorganic compounds. Unlike the phosphorus, its biological utilization is not known. Recent results however indicate that arsenic may be a micronutrient for certain marine organisms (Le Blanc and Jackson, 1973). Marine animals concentrate this element in variable proportions. Sometimes the concentration factor is as high as 3300 (Halstead, 1973). These interesting features perhaps reflect on its concentration levels in the sea in relation to place and time. The results of the present study given as preliminary account on the distribution of arsenic in the waters of Goa coast indicates that a comprehensive study on the arsenic cycle in sea water and estuaries would be worth undertaking.

Arsenic mainly occurs as arsenate in sea water (64 to 80%) (Johnson and Pilson, 1972), and in small concentrations as arsenite. In the coastal and estuarine waters of Goa, arsenate was found to be dominant (80 to 100%). The high concentrations in the estuarine and coastal waters appear to be the effect of

TABLE I
Distribution of arsenic in the coastal and estuarine waters around Goa

Station Nos.	Date	Soluble inorganic-As ($\mu\text{g/l}$)	
		Surface	Bottom
<i>Zuari estuary</i>	23-3-73		
9		16.11	30.53
10		2.97	18.65
11		66.57	30.10
12		47.91	43.25
<i>Off Pernem</i>	4-4-73		
1		< 1	< 1
2		< 1	< 1
3		1.70	13.14
4		10.17	11.70
<i>Off Colva</i>	12-4-73		
15		14.41	40.28
16		2.92	9.33
17		2.97	33.49
18		3.09	11.47
19		7.25	43.25
20		16.11	7.63
<i>Off Colva</i>	28-4-73		
15		< 1	< 1
16		5.60	1.69
17		9.75	15.69
18		5.68	2.12
19		< 1	3.77
20		< 1	36.46
<i>Off Aguada</i>	3-5-73		
5		< 1	< 1
6		< 1	< 1
7		< 1	< 1
8		< 1	< 1
<i>Off Mormugao</i>	7-5-73		
13		< 1	< 1
14		< 1	< 1
15		< 1	< 1

adjoining land. Large variations observed at various locations reflect on its chemical instability and much of it appears to be lost to the sediments by way of precipitation and adsorption. This is evident from the relatively high values found at the bottom layers. The other evidence that it might have been lost to the bottom layers could be inferred from the extremely low surface concentrations ($< 1 \mu\text{g/l}$) found off Aguada and Mormugao (Table I), as compared with the high concentrations found in the estuarine waters. Similar feature is also observed in the case of iron which is in very high concentrations at the surface in the estuaries and low in the coastal waters. It is presumed that iron gets lost at the bottom or in the sediments as a result of precipitation at the prevailing pH of sea water and also by flocculation (Kamat and Sankaranarayanan, 1974). For arsenic, it is quite likely that it is partly carried to the bottom waters and sediments by adsorption on ferric hydroxide and partly during flocculation. The presence of significant concentrations of arsenic further north and south indicates that the arsenic released from the sediments by chemical and bacterial agencies

enters the upper layers. Much of the arsenic seems locked up in the sediments and relatively higher concentrations in the bottom waters suggest active recycling of this element. Some observations made during the monsoon period in the estuaries show high surface concentrations of arsenic as compared to those during the other period. These confirm that much of the arsenic is of land origin. From Goa, large quantities of iron ore are mined and shipped to other countries and there is a possibility of some arsenic associated with iron (perhaps as FeAsS) leaching into the rivers during the monsoon period. Further studies on the distribution of arsenic extending to wider area and also its complete biogeochemical involvement at few selected locations will elucidate the nature and role of arsenic in the offshore, coastal and estuarine waters along the Indian coast.

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