

**STUDY OF ARSENIC AND RELATED PARAMETERS ALONG
THE CENTRAL WEST COAST OF INDIA**

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**by
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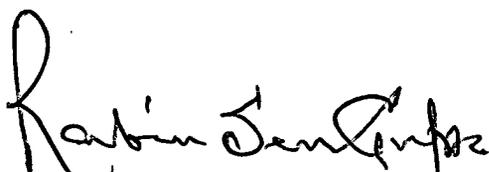
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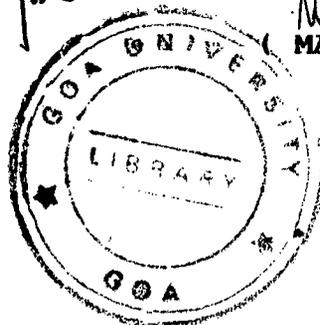
June 1994

**TO MY
PARENTS**

STATEMENT

As required under the ordinance 19.8 of the Goa University, I state that the present thesis entitled "Study of arsenic and related parameters along the Central West Coast of India" is my original contribution and the same has not been submitted for any degree of this or any other University on any previous occasion.


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CHAPTER - I

INTRODUCTION

I. INTRODUCTION

I.1 OCCURRENCE

Arsenic occurs in nature as 'scherbenkobalt' but is found in the form of its compounds. The most important of these are its compounds with the metals (the arsenides), which usually occur in isomorphous mixture with sulphides. The most commonly found form is arsenopyrite (mispickel), an isomorphous mixture of FeS_2 and FeAs_2 , usually with the approximate composition FeAs_2S . Pure iron arsenide, FeAs_2 , occurs as arsenical pyrites or lollingite. Naturally occurring sulphides of arsenic are realgar, As_4S_4 and orpiment As_2S_3 . The oxides As_2O_3 (flowers of arsenic, arsenolite) is found as a product of weathering of arsenical ores. In general arsenic is so widely distributed in nature that metals prepared from sulphide ores are almost invariably arsenical, and it is a matter of considerable difficulty to free them completely from arsenic.

Arsenic is another of the chalcophile elements which is accumulated in sulphide deposits. It is found in concentrations of up to 1% in lead-zinc

concentrations used in smelters and because of its volatility (sublimes at 650 °C) it can be readily distributed into the atmosphere. Perhaps the largest sources of pollution from this element are agricultural chemicals such as herbicides, fungicides, rodenticides, and insecticides.

In its toxicology, arsenic is a cumulative poison which inhibits-SH groups in enzymes. Chronic poisoning leads to loss of weight, loss of appetite with accompanied gastrointestinal disorders similar to gastroenteritis. With an average concentration in the earth's crust of 1.5 to 2 mg/kg, Arsenic ranks 20th in abundance in relation to other elements (NAS 1977). It is present in rocks and ores and is found native in the sulphides realgar (As_2S_3) and orpiment (As_2S_3) as arsenides and sulpharsenides of heavy metals, as the oxide and as arsenates, Mispickel or arsenopyrite (FeSAs) is the most common mineral.

Oxide forms of arsenic are usually found in sedimentary deposits. The elemental oxidation state though stable in reducing environments is rarely found.

Soils contain 4mg/kg of arsenic with an average background level of about 7 mg/kg.

The arsenic concentrations of fresh waters in unpolluted areas vary, but typical values seem to be a few micrograms per liter or less. Quentin and Winkler (1974) found an average value of 3 ug/liter in river water and 4ug/liter in lake water in Federal Republic of Germany. Mean arsenic concentration of 0.02 to 1.05 ug As/liter were reported for some Norwegian rivers (Lenvik et al 1978). The relative importance of the particulate-bound, complexed and dissolved components in river-borne arsenic is variable (Ferguson and Gavis, 1972; DeGroot 1973; Crecelius et al 1975, Waslenchuk and Windom 1978; Langston, 1980; Lemmo et al 1983).

G. H.

Arsenic is present in sea water predominantly as arsenate and at the pH and Eh of normal sea water will be partially protonated ie it will exist as HAsO_4^{-2} (Ferguson and Gavis, 1972). Other forms of arsenic are present in sea water as a result of biological mediation. Arsenic has a rich and complex organic chemistry and this is reflected to some extent in its environmental behaviour.

Arsenic has been long known as a poison and a therapeutic agent. Arsenious oxide (As_2O_3) is the starting point for manufacture of other arsenicals used as pesticides, herbicides, cotton desiccants and wood preservatives, in the manufacture of glass, ceramics, semi-conductors and dyestuffs, and as additives in alloys to increase hardness and heat resistance.

I.2 SOURCES:

Much of the arsenic is intentionally released into the environment (eg pesticides). Arsenic is also released unintentionally as a result of smelting or roasting sulphide minerals, the combustion of fossil fuels, leaching of exposed wastes from mining activities and accelerated erosion of land. Volcanoes, the burning of vegetation and continental weathering are major natural contributions of arsenic to the environment. It has been considered though, that releases resulting from the activities of man may exceed those due to natural processes (Ferguson and Gavis 1972, Mackenzie et al 1979). There is still uncertainty about the relative importance of the various sources of arsenic (Walsh et

al 1979; Chilvers and Peters, 1984). Ferguson and Gavis (1972) considered that the influence of the increase in arsenic concentrations in a well mixed ocean would be negligible for many thousands of years. However, Mackenzie et al (1979) calculated a net gain by oceanic waters of $5.66 \cdot 10^4$ tons/ year. A similar result has been obtained by Chilvers and Peters (1984). They calculated a net gain in the arsenic contents of the oceans of $13.7 \cdot 10^4$ tons/year, which represents a concentration increase of 0.1% per year. Aspects of the global flux of arsenic have also been considered by Walsh et al (1979). The most important local inputs of arsenic into the marine environment result from the smelting of non-ferrous ores and from the river drainage of areas with substantial arseniferous ore deposits. Various local sources of arsenic contamination to the marine environment have received attention in the literature. The largest of these was a copper smelter which discharged liquid waste and crystalline slag particles into the Puget Sound in north western Washington state, U.S.A. (Crececius et al;1975).Lindau (1977), Hallberg (1979) and Klumpp and Peterson (1979) and Penrose et al (1975) measured the distribution of elevated levels

of arsenic in water, sediments and organisms affected by drainage from areas of mining and land containing arseniferous ores in south-west England and Newfoundland, Canada, respectively. Rivers draining large industrial areas are also likely to carry increased arsenic burdens from a variety of industrial and domestic sources, for example, the Rhine contains arsenic at a concentration five times as high as oceanic water (Weichart 1973). Localized emissions of the type documented by Ambrosi and Amicarelli (1982) when several tons of arsenic were accidentally released, are no longer thought to be a significant source.

I.3 TRANSPORT:

Arsenic enters the oceans from the atmosphere and in freshwater it is associated with particulates and the dissolved phase (De Groot, 1973; Crecelius et al, 1975; Waslenchuk and Windom, 1978). Langston (1980) reported that arsenic entered estuaries in particulate form from weathering of ores such as arsenopyrites and as arsenate and arsenite which may be scavenged by hydrated iron oxides in estuarine sediments. However arsenic borne by

rivers of south-eastern U.S.A. was complexed to low molecular weight dissolved organic material and passed through the estuaries without being precipitated (Waslenchuk and Windom, 1978). The precipitation of arsenic entering natural waters by hydrated ferric compounds has also been considered by Ferguson and Gavis (1972) and Lemmo et al (1983). Arsenic in oceanic waters is predominantly in dissolved form (Johnson and Pilson 1972; Gohda, 1975), although it may be removed from solution by adsorption or co-precipitation with iron and aluminium compounds (Crececius et al 1975; Andreae, 1979). As the distribution of total arsenic levels in the oceans show little variation, movement of arsenic with bodies of water will have little or no effect on the overall total arsenic distribution. However, the biologically facilitated transport of the various arsenic species in sea water may have some effect on the overall arsenic distribution within a certain locality (Johnson and Pilson, 1972; Andreae, 1978; 1979; Peterson and Carpenter, 1983).

I.4 TRANSFORMATION:

Transformations of arsenic in the marine environment are biochemically mediated with the exception of arsenite - arsenate conversion facilitated by the oxic- anoxic status of the water. Four species of arsenic (arsenite, arsenate, monomethylarsonate, dimethylarsinate) have been detected in sea water (Braman and Foreback, 1973; Andreae, 1978; 1979) and although in oxic waters arsenate predominates, arsenite is always present at greater than thermodynamic equilibrium concentrations (Johnson and Pilson, 1972; Andreae, 1978; 1979). Johnson (1972) and Johnson and Burke (1978) have demonstrated the ability of bacteria to reduce arsenate in sea water to arsenite. Evidence that marine waters of the photic zone contain arsenite, monomethylarsonate and dimethylarsinate indicate that algae play a major role in the production of reduced and methylated forms of arsenic in sea water (Andreae, 1978; 1979; Andreae and Klumpp, 1979; Sanders and Windom, 1980). Other organisms may also transform arsenate to arsenite and/or simple methylated forms (Pilson, 1974; Vidal and Vidal, 1980). Sanders (1979a) and Scudlark and

Johnson (1982) have also shown a microbial role in the demethylation and oxidation of methylated arsenicals in sea water. Thus all stages in the sequence arsenate --> arsenite ----> $\text{CH}_3\text{As}(\text{OH})_2$ ----> $(\text{CH}_3)_2\text{AsO}_2\text{H}$ have been shown to involve possible biological mediation.

Much work have been carried out in an effort to identify arsenic compounds in marine organism as well to understand the mechanism for their formations (Lunde 1975, 1977; Penrose et al, 1977; Wrench et al, 1979; Cannon et al, 1981; Edmonds et al, 1982a; Edmonds and Francesoni, 1981a; 1983). Laboratory experiments carried on marine animals have shown that food is more important as a source of arsenic than sea water. Therefore the precursors of arsenobetaine, the major form of arsenic in marine animals at the top of the food chain is most likely formed along the food chain. The analysis of biota associated with sargassum weed indicated that substantial amounts of arsenic were present in forms other than the inorganic or methylarsenic compounds (Johnson and Braman, 1975). Only small amounts of simple methylated arsenicals were present. Water soluble and lipid soluble forms of organic arsenic have both been

detected in algae, their relative proportions varying in different forms of algae (Irgolic et al, 1977; Cooney et al, 1978; Klumpp and Peterson, 1981). Identification of organic arsenic compounds other than the methylated arsenic acids in algae is to date confined to arsenic containing derivatives of ribofuransoide (ACR) isolated from the brown kelp Ecklonia radiata (Edmonds and Francesoni, 1981b, 1983). Acylation by chain fatty acids of the relevant free hydroxyl groups in the appropriate ACR would produce a phospholipid analogous to lecithin (Edmonds and Francesoni, 1983). Thus lipid soluble as well as water soluble ACR derivatives may exist.

Arsenobetaine has been found to be the major form of arsenic in marine animals contributing to the human diet e.g. western rock lobster, dusky shark (Cannon et al, 1981), American lobster (Edmonds and Francesoni, 1981a), several teleost fishes, crabs and shrimps (Luten et al, 1982; Norin and Christakopoulos; 1982; Luten and Riekwel, 1983; Shiomi et al, 1984). Arsenobetaine is the arsenic analogue of betaine a common osmolyte in marine organisms (Yancey et al, 1982).

I.5 ACCUMULATION

Marine algae contain arsenic at concentrations 2000 to 5000 times greater than those in sea water. Uptake of arsenic by the brown macroalgae Fucus spiralis and Ascophyllum nodosum was found to increase in direct proportion to increasing temperature and was greater in the presence of photosynthetic inhibitors or in the dark than under illuminated conditions (Klump, 1980a). Fucus spiralis accumulated four times more arsenate than arsenite. Uptake will therefore be affected by the prevailing physical and chemical conditions of the sea water notably its oxic- anoxic status. However, Klump (1980a) showed that variation of pH or salinity did not affect arsenic incorporation. The accumulation of ⁷⁴As reached a steady state in 1 to 8 days, depending on the species and external arsenic concentration. At steady state the accumulated arsenic was proportional to the external arsenic concentration. Sanders and Windom (1980) also found that arsenate uptake depended on the concentration present in the media, both in terms of the uptake rate and the total arsenic absorbed, for the



phytoplankton Skeletonema costatum. In addition uptake and total arsenic absorbed were affected by the phosphate concentration of the media in S. costatum which suggested to Sanders and Windom (1980) a common mechanism of phosphate and arsenate uptake. Klumpp (1980a) found no evidence for this in his studies with macroalgae, although high concentration of phosphate (40 to 400 μM) initially inhibited arsenate uptake.

Klumpp (1980b) reported that when marine snails Littorina littorea and Nucella lapillus were held in sea water containing 3 $\mu\text{g/liter}$ radio-labelled arsenate (approximately the normal ocean water concentration), they achieved steady state tissues. As concentrations two orders of magnitude below the actual arsenic levels in nature. Fowler and Unlu (1978) concluded as a result of experiments with radio-labeled arsenate that levels of arsenic in the shrimp Lysmata seticaudata would be difficult to achieve by the direct absorption of arsenic from water and concluded that food is the means by which shrimp accumulate arsenic in the natural environment. They supported this hypothesis with data showing a high degree of assimilation and long retention of arsenic

ingested by shrimp from food. Pentreath (1977) studied the accumulation of ⁷⁴As- labelled sodium arsenate from sea water by plaice (Pleuronectes platessa) and thornback ray (Raja clarata) and made comparisons with accumulation of arsenic from labelled food. He found that accumulation direct from sea water was slow. In contrast retention of ⁷⁴As from labelled food was high for the ray (85%) but low (10%) for the plaice. Both these species contained the largest fraction of the ⁷⁴As body burden in muscle. However it is most unlikely that fish would receive food containing arsenic as arsenate in natural circumstances.

It is possible, in the light of general conclusions about the importance of food versus water to arsenic accumulation, that detailed kinetic studies of absorption from water by marine animals will have little relevance to natural situations. Nevertheless, Klumpp (1980b) showed that a number of environmental factors influenced the uptake of arsenic by marine snails. The uptake of arsenic by Littorina littorea was reduced at low salinity and by phosphate levels between 9 and 17 μM^{-1} , and increased by higher temperatures and arsenate

concentrations. However, the uptake of arsenic from water by Lysmata seticaudata (Fowler and Unlu;1978) was greater at low salinities. Large individual variations masked any effect that temperature might have had on accumulation. Unlu and Fowler (1979) showed that the absorption of arsenate by the mussel Mytilus galloprovincialis increased with increasing concentration of arsenic in the water, increased with higher temperatures and was three times as high at a salinity of 19×10^{-3} than at 38×10^{-3} . Arsenic is not biomagnified in marine food chains (Ferguson and Gavis, 1972; Kennedy, 1976; Klumpp and Peterson, 1979; Sanders, 1980; Klumpp, 1980b). Nevertheless, a number of studies have demonstrated positive relationships between size of marine animals and their arsenic concentrations indicating that several species are able to bioaccumulate arsenic. Bohn (1975) reported significant relationships between fish size and arsenic level for wolf fish (Anarhichas minor), halibut (Reinhardtus hippoglossoides) and shortthorn sculpin (Myoxocephalus scorpius) from west Greenland. Kennedy (1976) demonstrated significant positive correlations between

animal size and arsenic concentrations for two species of pandalid shrimps (Pandalus borealis and Pandalus montagui) from several localities in Newfoundland and Labrador (Canada). Bohn and McElroy (1976) and Bohn and Fallis (1978) reported similar relationships for arctic cod (Boreogadus saida) and shortthorn sculpin (Myxocephalus scorpius), respectively, from northern Canadian waters. A teleost fish (Sillago maculata) from Cockburnsound, western Australia was shown to display a positive relationship between size and arsenic level (Edmonds and Francesconi 1981c). Bohn (1975) and Klumpp and Peterson (1979) have shown elevated levels of arsenic in biota from areas of abnormally high environmental levels. Langston (1980) showed that concentrations of arsenic in estuarine organisms correlated more significantly with the As/Fe ratio in sediments than with arsenic levels alone.

CHAPTER – II

DESCRIPTION OF THE STUDY AREA
AND REVIEW OF EARLIER WORK

II. DESCRIPTION OF THE STUDY AREA AND REVIEW OF EARLIER WORK

II.1 STUDY AREA

II.1.1 The State of Goa

Goa is the 25th state of India. It lies midway along the west coast of India and covers an area of about 3700 km² with a population of little over one million. It is bordered by the states of Maharashtra on the north and Karnataka on the east and the south. It has a coastal stretch of about 100 km. About 36% of the total area of Goa is used for agriculture, 25% under forest cover, 14% under mining and the remaining are residential areas.

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 which is about 68% of the total geographical area of Goa. It is estimated that about 55% of the population of Goa is benefited by these rivers. They flow through the mining areas and are heavily used to transport iron and manganese ores to the Marmugao harbour. In fact 90% of the states iron and ferromanganese ores are transported through these

estuaries in barges. In addition they provide a cheap mode of transportation to the people, apart from being the only source of fish during monsoon when fishing activities in the open sea are suspended due to rough weather.

The Mandovi and Zuari estuaries are the main waterways of Goa and are of utmost importance for the economy of the territory as they flow through mining areas opening into the Arabian Sea. The mouths of the two estuaries are separated by a promontory between them at Cabo. Developmental activities are more along these two river basins as compared to the rest of the territory. This estuarine system is extensively used for aquaculture and recreational pursuits.

These, being tidal-stream estuaries, are more or less homogenous from surface to bottom during the non-monsoonal months when fresh water flow is insignificant. The well mixed character prevailing in this period results in low Richardson's number, indicating turbulent mixing, as well as high horizontal longitudinal dispersion coefficients from top to bottom (N.I.O,1979).

With the onset of the south-west monsoon increased fresh water inflow results in stratification between the upper-most and the subsurface layers. The average depth of both the Mandovi and Zuari estuaries is around 6m.

About 2/3 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. They are mainly transported in barges across these estuaries to the harbour (mouth of Zuari) for export. Further non-mechanized fishing is intense in these estuaries particularly during the south-west monsoons. All these factors introduce suspended load, industrial effluents petroleum hydrocarbons and domestic sewage into the estuaries, creating additional stress to the ecosystem. The topography and consequently the hydrographical conditions of both the estuaries are different.

II.1.2 River Mandovi

The Mandovi river originates from the Parwa ghat of the Karnataka part of the Sahyadri hills and after traversing a stretch of about 70km joins the Arabian Sea

through the Aguada bay near Panaji. Its width at the mouth is 3.2km while in the upstream it narrows down to 0.25km. It is also fed by monsoon precipitation and discharges from a catchment area of about 1150 km². Its pre and post-monsoonal flows (about 0.6 km³/year) are also regulated by the semidiurnal tide having a similar amplitude. However, the Mandovi has a large tributary system and along its course has a number of islands, sharp turns, shallow depths and lower average salinity. From a maximum of 67km in May, the salinity intrusion (marked by 1 ppt isohaline) comes down to a minimum distance of about 10 -11 km in June which persists through July. The estuary is well mixed when fresh water run off is reduced to lower levels. During the monsoon, formation of salt wedge has been observed near the mouth of the river (Qasim and Sen Gupta, 1981).

The two estuaries are inter connected by the narrow Cumbarjua canal about 11 km and 14 km away from the mouth of the Zuari and Mandovi estuaries respectively demarcating the island of Panaji in between. The canal is about 17 km in length and 0.5 - 0.7 km in width, and bordered by thick mangrove vegetation on the northern

fringe. It is narrow and shallow at the Mandovi end and appreciably wider and deeper at the Zuari end. This canal forms an interesting example of two estuaries interconnecting through a common canal. Flow pattern through the canal is mainly regulated by the tidal influence at the Zuari end. During the monsoon all boat and barge traffic is diverted along this canal and thus it becomes the most important waterway during that period.

The river Mandovi carries discharges from a catchment area of 1150 km^2 . The river basin has an area of $\sim 380 \text{ km}^2$ and the average annual fresh water runoff has been approximated to 16 km^3 . The summer runoff is about $0.06 \text{ km}^3/\text{year}$ (TCPD, 1978). The river is navigable to about 42km from its mouth (close to #6) which is also the last loading point for the ore carrying barges. The river carries drainage from 435 km^2 of forest land. About two-thirds of the total mining activities in Goa are located along the Mandovi basin. There are 27 large mines which 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 catchment area of 550 km^2 . The average annual freshwater run-off has been approximated to 9 km^3 . The summer run-off is about $0.03 \text{ km}^3/\text{year}$ (TCPD, 1978). The river is navigable to about 62 kms from its mouth and the last loading point for the ore carrying barges is about 50 km^2 (close to Z-6). The river carries drainage from 309 km^2 of forest land. Ten large mines located in this basin generate 1000 - 4000 tons of rejects per day per mine, a good amount of which can be expected to be added to the river. Mining activities are about double as much along the Mandovi basin as they are along the Zuari basin, while industrial activities, as can be judged from the volume of effluents are much more intense in the latter than in the former. The population in both the basins being almost the same with similar proportion between urban and rural categories, the difference in the volume of domestic sewage added to both the river is not very significant.

II.1.3 River Zuari

The river Zuari originates from the Dighi ghat of the Karnataka part of the Sahyadri hills and after flowing through a stretch of about 67 km meets the Arabian sea near the Marmugao - Dona Paula point. Its width at the mouth of the estuary is 5.5km while, upstream it narrows to less than 0.5km. It is fed by the monsoon precipitation and also receives discharges from a catchment area of about 550km². The quantity of fresh water discharge during the pre and post-monsoon periods is negligible (about 0.03 km³/year) and therefore the flow during these seasons is regulated by tides of semi-diurnal type having a spring amplitude range of 2.3m. Maximum distance of penetration of 0.5 X 10⁻³ chlorinity (~0.9 X 10⁻³ salinity) upstream is about 65km away from the mouth during May. It gets reduced to a minimum of 20km during June and July following the onset of the south-west monsoon. The Zuari is well mixed when fresh water run off is minimum. During the monsoon salt wedge formation has been observed near the mouth of the estuary as well as in the mid channel up to a distance of 14km from the mouth (Qasim and Sen Gupta, 1981).

II.1.4 The mining industry

The backbone of the economy of Goa is the mining industry producing manganese and ferromanganese ores. It started during the early fifties, but the production picked up during late fifties and the export, increased. Mining accounts for about 32% of the country's iron ore production and 55% of India's export. During 1984 - 85, mining had been carried out in 149 mines which is about 14 % of the surface area of Goa. From the mines the ores are transported to the loading points on the banks of the rivers by trucks and conveyer belts. These ores are transported to the harbour by barges. There are about 215 barges plying in these rivers carrying ore from the loading point on the banks of the rivers to the ships in the harbour. 65% of the total ore produced are from the northern part of the territory and the rest from the southern part. The ore produced in the northern part is transported along river Mandovi, and the other part is along the river Zuari. It has been estimated that the production of one tonne (t) of iron ore generates about 1.5 t of rejects and that about 25 to 30 million tons of mining rejects are being generated every year (NIO,

1979). These rejects mostly laterite, aluminous clay, brown clay etc alongwith low-grade iron ores are dumped mainly on the hill slopes which may find its way into these rivers during monsoon. In addition, the tailings from the processing plants will be reaching the rivers during all the seasons. Air borne particles during loading and spillage during transport also contribute.

II.1.5 Meteorological features

The atmospheric temperature of Goa varies between 15° and 39° C, the maximum being in April-May and minimum in December-January (D'Souza, 1983). The monsoon cycle is the major factor which influences the hydrographical features of Mandovi and Zuari estuaries as in the case with other estuaries along the west coast of India. Based on this, the year has been divided into three seasons viz., premonsoon (Feb-May), monsoon (June to September) and post-monsoon (Oct-Jan). Generally maximum rainfall occurs from June to August tapering off to the post monsoon. Premonsoon is practically dry. This classification is a generalized one and the length of the seasons vary from year to year depending on the

onset, intensity and duration of monsoon.

The longterm average rainfall in Goa is 2611 mm/year. The bulk of the rainfall is due to southwest monsoon and about 90% of the total annual rainfall occur during June-August. The average rainfall in the two river basins varies from 3000 mm downstream to 3730 mm at their uppermost regions.

II.2 REVIEW OF THE EARLIER WORK

There has been considerable interest in the understanding of the intricate processes taking place in estuaries such as their ecology, dynamics, chemical and geological and other related aspects. A considerable amount of work has been done in different aspects of estuaries to understand the processes happening in them.

The Mandovi and Zuari estuaries are the two important estuarine systems on the West Coast of India. Different aspects of Mandovi and Zuari have been worked out since 1970 after the National Institute of Oceanography was established in Goa. Some of the important work carried out in this estuarine system is

discussed below.

Physical Aspects

Hydrography and environmental characteristics were worked out by Dehadrai (1970 a,b). Sankaranarayana and Jayaraman (1971), Das et al., (1972), Murthy and Das (1972), Antony et al., (1974), Cherian et al., (1974, 1975), Kamat and Sankaranarayanan (1975a,b), Varma and Rao (1975), Murthy et al., (1976), Rao et al., (1976), De Sousa (1977), Sankaranarayanan et al., (1978), Qasim and Sen Gupta (1981), De Sousa et al., (1981).

Biological Aspects

Studies on the various aspects of phytoplankton production were carried out by Dehadrai and Bhargava (1972) Bhargava (1973), Bhargava and Dwivedi (1974, 1976), Bhattathiri et al., (1976) Pant et al., (1976), Bhargava et al., (1977), Devassy and Bhargava (1978) and Verlencar (1984). Studies on zooplankton were carried out by Goswami and Singbal (1974), George and Goswami (1977), Goswami and Selvakumar (1977), Selvakumar et al., (1977), Nair and Selvakumar (1979), Goswami et al., (1979), Goswami and George (1978), Goswami (1982) and

Achuthankutty and Nair (1983). Benthic studies were carried out by Parulekar and Dwivedi (1973, 1974), Parulekar et al., (1975), Harkantra et al., (1977), Parulekar et al., (1978) and Ansari et al., (1986), Desai (1988). D'Sousa and D'Sousa (1979) worked on the role of yeasts in the nitrogen budget in the estuarine sediments. Other biological studies include those of Lokabharati and Chandramohan (1985) and Saxena et al., (1988) on bacteria, Jagtap (1987) on organic matter and Wafar (1987) on mangroves.

Geological aspects

Rajamanickam and Shetty (1973) worked on the distribution of phosphorous and organic carbon in the nearshore sediments of Goa. Veeraya et al., (1973) studied the effects of artificially dumped material on some part of the coast of Goa. Textural characteristics of the sediments of the Marmugao harbour was studied by Rao and Rao (1974). Mehta et al., (1983) worked out the sediment dynamics in the Cumbarjua canal with the suspended load and settling current study. Phosphorous retention capacity of sediments of Mandovi estuary was

worked out by Rajagopal and Reddy (1984). Shirodkar and Sengupta (1985) worked on the behaviour of boron, calcium and magnesium in the industrial water of the Mandovi estuary.

Chemical Aspects

Diurnal variations of some physico-chemical factors of Zuari and Mandovi estuaries were studied by Singbal (1973, 1976). Arsenic content in these estuaries were worked out by Fondekar and Reddy (1974, 1975), Fondekar (1977). Solimabi and Naqvi (1975) worked on the alginic acid content of some sea weeds of Goa. Solimabi and Das (1977) worked on the distribution of iodine in marine algae of the Goa region. Naik (1978) worked on the calcium and magnesium concentrations of near shore waters of Goa. Rajagopal et. al., (1981) worked on the distribution of boron in the Zuari estuary. Studies on calcium, magnesium and sulphate were made by Sen Gupta and Naik (1981). Chemical characteristics of the Mandovi and Zuari were studied by D'Souza (1983). D'Silva and Rajendran (1983) worked on vitamin B₁₂ concentrations in the Mandovi estuary. D'Souza and Kamat Dalal (1981)

worked on the behaviour of fluoride in these estuaries. George et al., (1984) worked on the speciation of cadmium, lead and copper in the Mandovi estuary. Shirodkar and Anand (1985) worked on the behaviour of Boron in Mandovi estuary. D'Souza and Sen Gupta (1986) worked on dissolved oxygen variations in these two estuaries. Alagarsamy (1988) worked on metals in sediments of Mandovi.

Work done on arsenic:

There have been major advances during recent years in the knowledge of the distributions and geochemical behaviour of trace metals in the ocean (Burton and Statham, 1982; Bruland, 1983). Information on arsenic in the open water column has been limited to a few areas. Andreae (1979) has given detailed information on the distribution and speciation of the element in the North-eastern Pacific Ocean. Studies on arsenic concentrations in sea water were carried out by Johnson (1971), Philipchuk (1974), Fondekar and Reddy (1974), Crecelius (1974), Godha (1975) and Braman and Foreback (1973). Braman (1975) reported the occurrence of four

arsenic species in natural water's : arsenate, arsenite, methylarsenic acid and dimethylarsenic acid. These findings involve methylation and reduction reactions. Such a cycle was also proposed by Wood (1973). Andreae et al., (1984) determined arsenic concentrations along the central axis of the Baltic sea from the Bornholm basin to the Gulf of Finland. Cornelis et al., (1990) determined arsenic concentrations in the Tyro and Bannock Basins (eastern Mediterranean).

The behaviour of arsenic in the estuarine environment has received comparatively little attention. Studied systems can be divided into those in which the principal arsenic input is of marine origin (Waslenchuk and Windom, 1978; Howard et al., 1984; Froelich et al., (1985) and those in which the river or estuary is the major arsenic source (Andreae et al., 1983 Knox et al., 1984; Millward and Marsh, 1986).

An understanding of the reactivity of chemical elements in estuaries is essential to the assessment of their riverine inputs to the ocean and to the validation of global geochemical models (Turekian and Wedepohl, 1961; Martin and Whitfield, 1983). This is especially

important for elements such as arsenic which exhibit contrasting distributions in different estuarine systems. Arsenic was found to be conservative in the south eastern U.S. estuaries (Waslenchuk 1977; Waslenchuk and Windom, 1978; Froelich et al., (1985) in Puget sound (Carpenter et al., 1978), and in Carbon river (Klumpp and Peterson, 1979; Byrd 1978). Non-conservative distributions involving removal and/or remobilization were observed in British estuaries such as the Tamar, Clyde, Restronguet Creek, Beaulieu (Langston, 1983; Howard et al., 1984) in Chesapeake Bay, U.S.A. (Sanders, 1985), Tagus, Portugal (Andreae et al., 1983) and in French estuaries (Seyler, 1985). Many authors have reported a correlation between arsenic and iron-rich phases in nodules, (Calvert and Price, 1977) and in marine sediments (Crececius et al., 1975; Neal et al., 1979; Langston, 1980; Marshall, 1983; Maher, 1984/85, Farmer et al., 1986, Farmer and Cross, 1979). Arsenic levels in sediments from Lake Biwa, Japan was reported (Takamatsu, et al., 1985); from Lake Ohakuri of New Zealand (Aggett and O'Brien, 1985) and Lake Washington, U.S.A. (Peterson and Carpenter, 1986). The

first study of arsenic speciation in marine pore waters was reported by Andreae (1979), while Peterson and Carpenter (1986) reported that arsenite, As(III), was the dominant species in pore waters. Edenborn et al., (1986 a) demonstrated that the diagenesis of arsenic involves simultaneous release of arsenic and iron at a subsurface depth, followed by its removal from pore waters. Holme et al., (1980) studied the rates of microbial degradation of arsenic species in sediments.

Only two reports are available on the arsenic levels in Indian estuaries. Fondekar and Reddy (1974) reported arsenic concentration of upto 0.57 $\mu\text{mol/l}$ in Zuari estuary. Similar concentrations were also reported by Zingde et al., (1976) in the estuarine and coastal waters around Goa.

Arsenate is known to be metabolized by bacteria, yeast (Vidal and Vidal, 1980) and algae (Andreae and Klumpp, 1979) and the link between biological activity and the presence of dissolved methylated arsenicals is well established (Andreae, 1978, 1979; Johnson and Burke, 1978; Sanders and Windom, 1980; Sanders, 1985; Howard et al., 1982; Chau and Wong, 1978; Fowler and

Unlu, 1978; Unlu and Fowler, 1979; Andreae, 1986; Howard et al., 1988).

Andreae (1989) studied arsenic concentrations and speciation in the rivers of the Schelde watershed, Belgium. Similar studies were also carried out by Huang et al., (1988) in the Huang He river, in the estuary of the river Beaulieu (Howard et al., 1984), and the Tamar estuary (Knox et al., 1984) .

II.3 OBJECTIVES

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 speciation and behavior of arsenic in the estuarine ecosystem. Such information is lacking from any estuary along the Indian Coast. Since the characteristic of the estuarine ecosystem are greatly influenced by the monsoon, a seasonal study will help to study the behavior of arsenic during estuarine mixing.

CHAPTER – III

MATERIAL AND METHODS

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III. MATERIAL AND METHODS

The Mandovi and Zuari estuarine systems are located between Latitude 15° 25'N - 15° 30'N and Longitude 73° 45'E-73° 59'E. In order to study the seasonal changes, monthly observations were made. Water samples were collected for pH measurements, salinity, nutrients and arsenic analyses. Sediment samples were also collected for total organic carbon, and total arsenic analysis. The area is strongly influenced by the south west monsoon and all coastal traffic beyond an imaginary line between Marmugao head and Aguada lighthouse is prohibited from June to September every year.

III.1 STATION LOCATION AND SAMPLING PROCEDURES:

Six stations were located in the Mandovi namely M-1, M-2, M-3, M-4, M-5, M-6 and six in the Zuari Z-1, Z-2, Z-3, Z-4, Z-5, and Z-6 (Fig. 1). Observations were carried out at these stations once every month from January to December 1988. Surface water samples were collected by a clean bucket and near-bottom samples by Niskin PVC water sampler. Sediment samples were

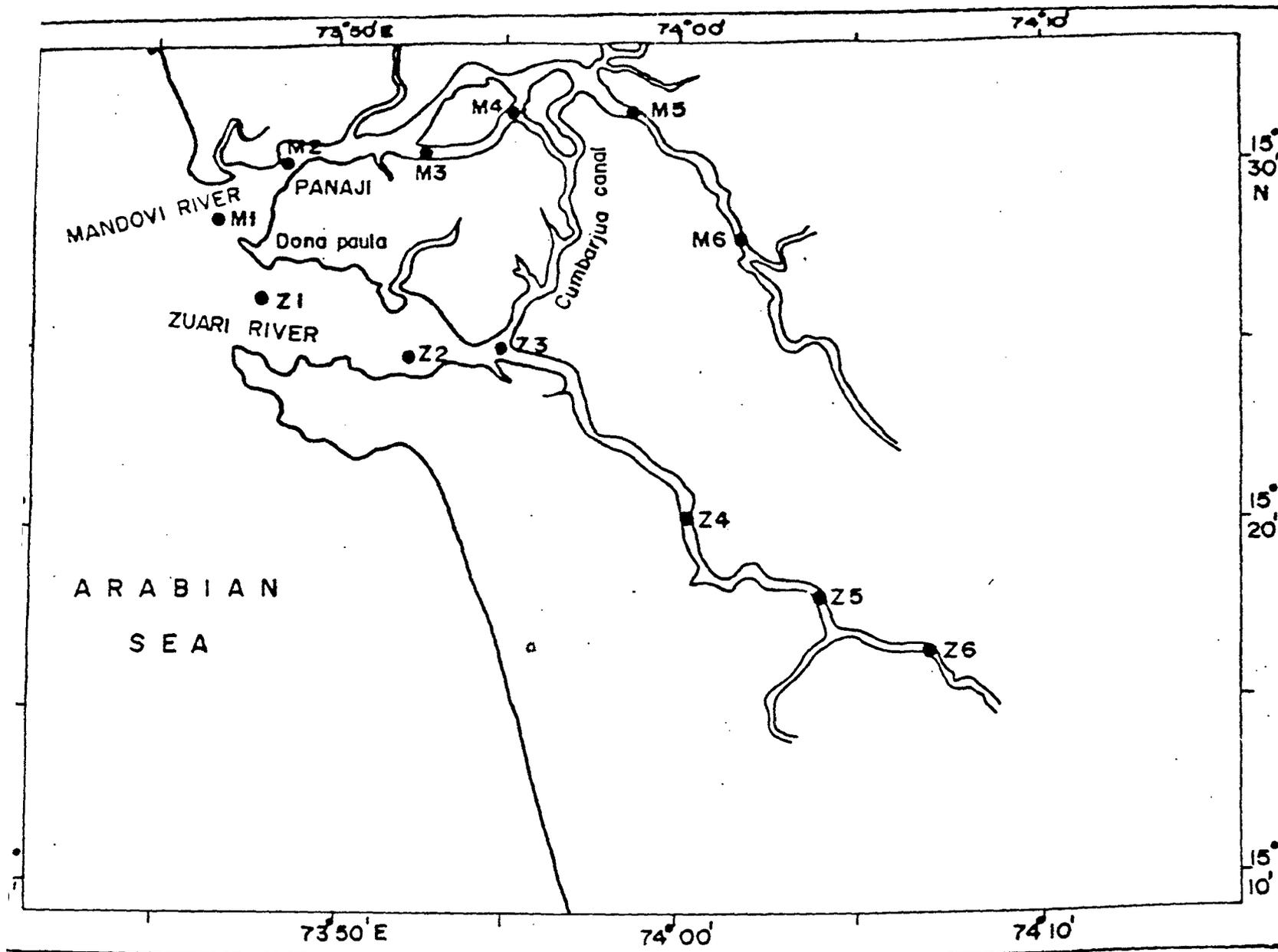


Fig. 1 Map showing sampling positions

collected using 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 lab where it was stored in a deep freeze until analysis could be carried out.

III.2 SAMPLING AND STORAGE OF WATER SAMPLES

Standard sampling and storage procedures (Grasshoff, 1976) were practiced throughout for the determination of all parameters.

Samples for dissolved oxygen were collected in glass bottles and immediately fixed with manganous chloride solution followed by alkaline iodide solution (Grasshoff, 1976). pH was determined on board the boat with 0.01 unit readability on Phillips model pH meter calibrated using standard buffer solutions (pH 7.00 and pH 4.00).

Samples were also collected in pre-cleaned

polyethylene bottles and transported to the shore laboratory in ice-boxes for the analysis of other parameters.

III.3 ANALYSIS OF WATER SAMPLES

II.3.1 Dissolved oxygen

Dissolved oxygen was determined using the popular Winkler's method (Grasshoff, 1976) in which oxygen in the sample was fixed with manganous chloride and alkaline iodide solutions. The dissolved oxygen was chemically bound in $Mn(OH)_2$ precipitate. Addition of dilute HCl liberated the bound oxygen which oxidized iodide ion to free iodine. The liberated iodine was titrated with standard thiosulphate. The relative standard deviation was $\pm 1.4\%$.

III.3.2 Chlorinity

Chlorinity of water was determined by titration with silver nitrate using potassium chromate as indicator as per the Mohr-Knudsen titration method and salinity was computed from chlorinity using Knudsen

hydrographic tables.

The standard deviations of chlorinity was 0.1% at high chlorinity and 0.05% at chlorinities less than 1×10^{-3} .

III.3.3 Silicate

Silicate was determined following the procedure outlined by Koroleff (1983). In this method acidified ammonium molybdate is allowed to react with dissolved silicate followed by addition of oxalic acid and ascorbic acid to reduce the complex into a strongly absorbing blue coloured compound. Absorbance was measured in 1 cm cell at 810 nm in a spectrophotometer.

III.3.4 Phosphate

Phosphate was analyzed following the standard modified procedure of Murphy and Riley (1962). Phosphate in solution reacted with acidified molybdate reagent to give yellow phospho-molybdate complex which was then reduced to a highly coloured blue compound with ascorbic acid. The colour was measured in 5 cm cell at

882 nm on spectrophotometer. Standard deviation was 3.6% at a concentration of 5 $\mu\text{mol/lit}$.

III.3.5 Arsenite and Arsenate

Arsenite and arsenate were determined at the shore laboratory in samples filtered through Millipore membrane filters applying the procedure outlined by Koroleff (1976). In this procedure a sum of total arsenic and phosphate is obtained by adding a small amount of iodate (to oxidize arsenite to arsenate) followed by phosphate reagents. In the second aliquot of sample a sum of arsenate and phosphate is obtained by adding phosphate reagents alone in the presence of reduced iodate solution. In the third sample aliquot of small amount of thiosulphate is added together with phosphate reagents. In the depths only the phosphate reacts. Individual arsenic species as well as phosphate concentrations are obtained from the differences between the set of three readings. Absorbance measurements were done on a spectrophotometer at 880 nm in a 10 cm cell. Blanks and standards were treated in the same manner. The relative standard deviation was 13% at arsenic

concentration of 0.8 μ g/l.

III.4 TOTAL ARSENIC IN SEDIMENTS

Total arsenic in sediments was determined by Atomic absorption spectrophotometry after hydride generation following the method of Andreae (1983 a). The analytical apparatus consisted of a Perkin-Elmer 2380 atomic Absorption spectrophotometer connected with a mercury hydride system (MHS-10). The absolute detection limit for the method is 0.02 μ g/l. Precision is estimated as +3 and 6%. | l

III.4.1 Total organic carbon in sediments

Total organic carbon in sediments was estimated using the method of El Wakeel and Riley 1957. During all analysis, high purity reagents were used throughout. Distilled or deionised water was used for the preparation of reagents, standard solutions and blanks according to suitability. Most of the methods were checked for reproducibility.

CHAPTER – IV

DISTRIBUTION AND BEHAVIOUR OF SUPPLEMENTARY PARAMETERS IN THE ESTUARINE SYSTEM

IV. DISTRIBUTION AND BEHAVIOUR OF SUPPLEMENTARY PARAMETERS IN THE ESTUARINE SYSTEM

IV.1 SALINITY

The average salinity values for each season are shown in (Fig 2,3) sharp seasonal variation in salinity are observed at stations M-1 to M-5 and Z-1 to Z-5, except at M-6 and Z-6 in both the estuaries. At the mouth of the river Mandovi, the salinity varied from 22.13×10^{-3} to 31.65×10^{-3} for the surface waters and from 22.19×10^{-3} to 30.23×10^{-3} for the bottom waters during the premonsoon period. During the monsoon it was low in general varying from 0.24 to 9.24×10^{-3} for the surface and 0 to 24.32×10^{-3} for the bottom waters, while during the postmonsoon the variation were from 4.25 to 30.10×10^{-3} for the surface and 6.31×10^{-3} to 27.63×10^{-3} for the bottom waters. Similar fluctuations for the Zuari estuary were 9.1 to 31.02×10^{-3} at the surface and from 0 to 30.72×10^{-3} at the bottom during the premonsoon period. During the monsoon it ranged from 0 to 13.81×10^{-3} for the surface and from 0 to 22.72×10^{-3} for the bottom waters. During the post monsoon the same were from 5.50 to 33.39 and

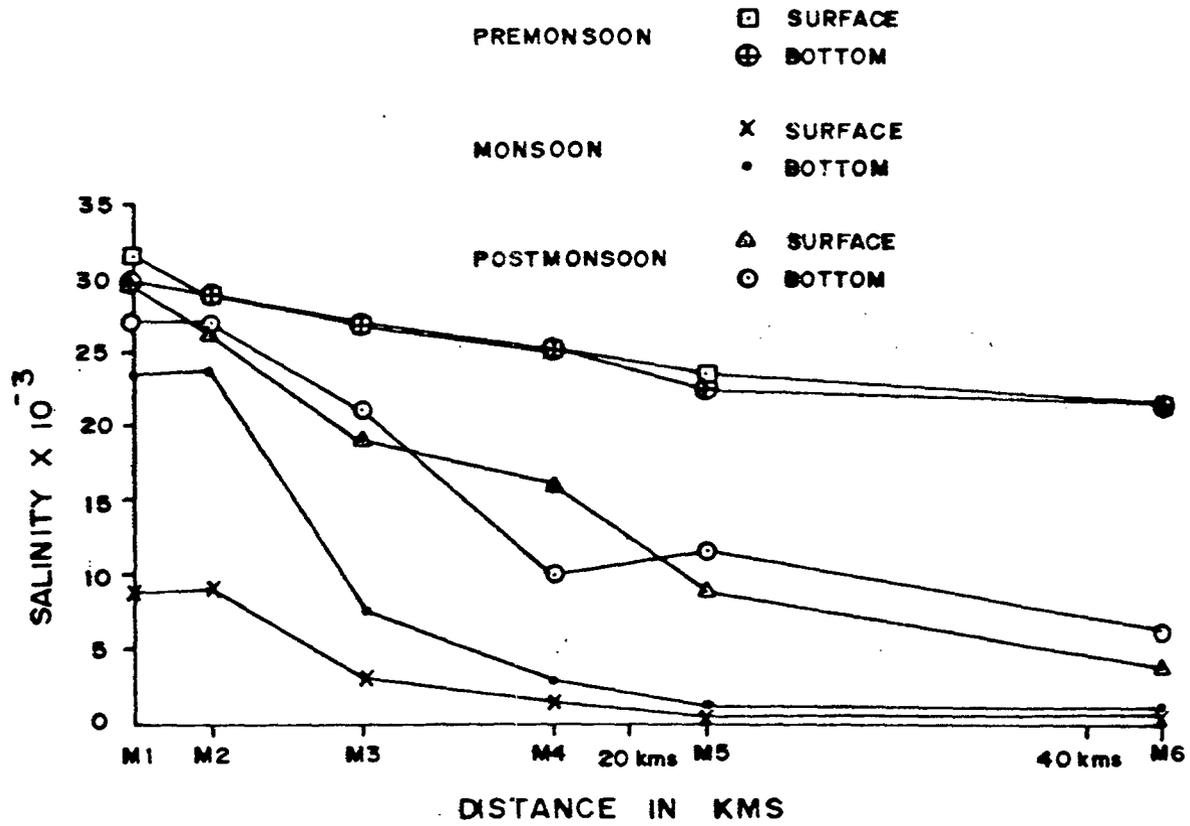


Fig. 2 VARIATION OF SALINITY IN MANDOVI

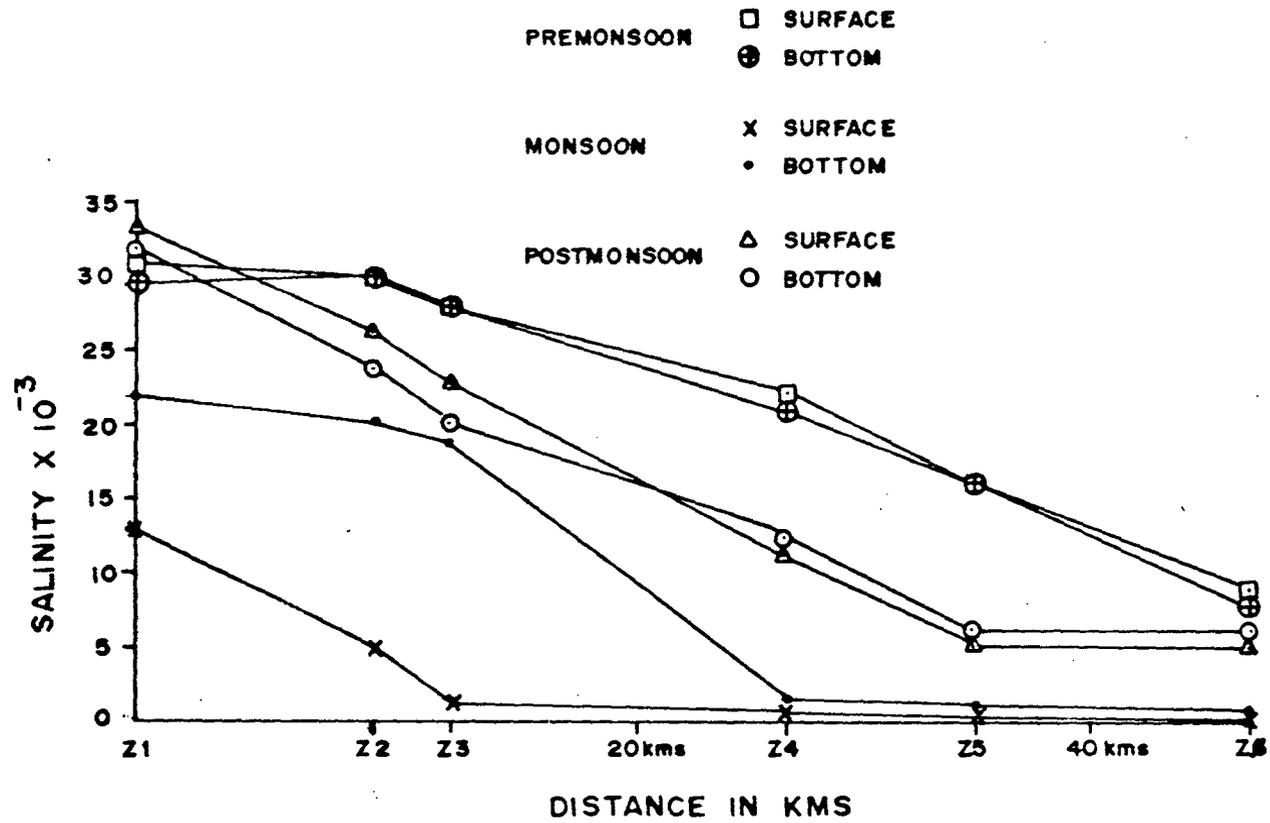


Fig.3 VARIATION OF SALINITY IN ZUARI

from 6.74 to 32.53×10^{-3} for the surface and bottom waters respectively. The present observation is in agreement with the observations of Devassy (1983), who recorded a wide range of salinity from freshwater zone (0.45×10^{-3}) and highly saline conditions (36.43×10^{-3}) at the mouth. Dehadrai (1970 a) also recorded a salinity range of 0.12 to 36.26×10^{-3} in the Mandovi-Zuari estuarine complex. Similar pattern was also observed by De Souza (1981) and Qasim and Sen Gupta (1981). They observed a large seasonal variation in salinity in both the estuaries. They reported salinity value of 35×10^{-3} from January to May for both Mandovi and Zuari estuaries. Sharp decrease was observed during the monsoon as expected. They reported that Mandovi-Zuari estuarine system can be classified as a coastal plain estuary which remains homogenous vertically for 8 months and gets moderately stratified for about 3-4 months during the year.

Upadhyay (1988) observed sharp seasonal variations in salinity in the Mahanadi estuary. The salinity reveals the increasing trend of salinity during premonsoon and postmonsoon, reaching the highest of

-3

about 32×10^{-3} in May and a sharp decline during the monsoon. Similar trend was also reported by Zingde et al., (1987) for the Narmada and Tapi estuaries.

Salinity decreased steadily upstream as expected all along the estuarine region reaching the freshwater end member. The salinity reveals increasing trend both during the postmonsoon and premonsoon, recording the highest of about 35×10^{-3} at the mouth of the estuaries in May and a sharp decline during the monsoons with minimum in the month of July. The differences in salinity of surface and bottom waters is quite significant, but being expectedly more in bottom water. The salinity of the surface and bottom layers increase downstream, so that there is a steady longitudinal salinity gradient over most of the estuary. Higher values of salinity ^{was} derived when conditions were optimum for increased net evaporation. Low values of salinity occurred with the occurrence of rainfall, land drainage and increased runoff from the river, causing a decrease in surface salinity during July and October. || P

In the premonsoon season the estuaries get well mixed from surface to bottom throughout their lengths. The freshwater flow is minimum and the salinity is maximum during this season. The extent of salt water intrusion into the estuaries varied seasonally in relation to the amount of freshwater discharge. During the premonsoon, the intrusion by salt water into the estuaries was deep and maximal in the month of May, the distance being 63 km in Zuari and 55 km in Mandovi from the mouth. During most part of the year salinity of the water in the lower regions of both the estuaries was almost equal to that of coastal sea water.

During the monsoon, due to heavy rainfall the estuaries become freshwater dominated. The surface water shows zero or near-zero salinities. Lowest salinities occurred from June to September, when the intensity of monsoonal runoff was the highest. In Mandovi salinity was lower than in Zuari due to its larger tributary system and greater catchment area. In July with high rainfall, salinity varied from 7.42×10^{-3} at station M-2 to 0 at station M-6. Similar trend was also observed in the Zuari estuary.

During the non-monsoon months when freshwater addition was insignificant the salinity was homogeneous from surface to bottom. During the premonsoon and postmonsoon months, the range narrows down. The near uniform value of surface and bottom water salinities during these period is attributed to the marine dominance of the estuary.

IV.2 DISSOLVED OXYGEN

High oxygen concentrations were observed at the mouth of the Mandovi and Zuari (4.43 and 4.38 ml/l). The surface and bottom water showed almost the same trend of variation in concentration with little difference from surface to bottom indicating that these estuaries are always well mixed except during the monsoon when the stations at the mouth of the estuary showed vertical stratification, with the surface water having higher concentration than the bottom waters. This was more prominent in the Mandovi than in the Zuari.

The concentration of dissolved oxygen showed a wide range of variation throughout the year. The average values of dissolved oxygen for each season is given in Table 1 and 2. In the Mandovi estuary the values for the surface water ranged from 3.73 ml/l to 4.45 ml/l, while it varied from 3.58 to 4.22 ml/l for the bottom waters.

In the Zuari estuary the dissolved oxygen values varied from 4.22 to 4.38 ml/l for the surface and from 3.81 to 4.19 ml/l for the bottom waters during the same period. In general the dissolved oxygen concentrations increased upstream along the estuarine system. The high dissolved oxygen values at the river end is because of the high solubility of the gas at lower salinities.

During the monsoons low values of dissolved oxygen were observed as compared to the other seasons. The values varied from 3.89 to 4.31 ml/l for the surface and from 3.81 to 4.04 ml/l for the bottom waters of the Mandovi. For the Zuari these were 3.69 to 4.27 ml/l and from 3.48 to 3.80 ml/l for the surface and bottom waters respectively. At higher salinities a slightly lower dissolved oxygen is generally expected because of lower

TABLE - 1

Average values of Dissolved Oxygen in Mandovi (ml/l)

	PREMONSOON	MONSOON	POSTMONSOON
<u>Surface</u>			
1) M-1	4.43	4.30	4.09
2) M-2	4.21	4.31	3.94
3) M-3	4.45	3.59	4.16
4) M-4	4.19	4.05	4.21
5) M-5	4.24	3.87	4.15
6) M-6	3.73	3.89	4.05
<u>Bottom</u>			
1) M-1	3.75	4.54	3.22
2) M-2	4.16	4.04	3.44
3) M-3	4.22	3.80	3.60
4) M-4	3.93	3.81	4.10
5) M-5	3.86	3.81	3.66
6) M-6	3.58	3.81	3.96

TABLE - 2

Average values of Dissolved Oxygen in Zuari (ml/l)

	PREMONSOON	MONSOON	POSTMONSOON
<u>Surface</u>			
1) Z-1	4.38	4.10	3.96
2) Z-2	4.38	4.14	3.84
3) Z-3	4.27	4.27	3.80
4) Z-4	4.22	3.94	4.21
5) Z-5	4.37	3.69	4.83
6) Z-6	4.22	3.76	4.67
<u>Bottom</u>			
1) Z-1	4.19	3.90	2.77
2) Z-2	4.16	3.80	2.95
3) Z-3	3.81	3.80	3.80
4) Z-4	3.60	3.49	3.91
5) Z-5	4.18	3.42	3.92
6) Z-6	4.12	3.48	3.55

solubility. During premonsoon the productivity is high (Devassy et al., 1978) leading to higher production of oxygen. Comparatively high values were observed during premonsoon suggesting the abundant growth of phytoplankton and related zooplankton leading to high biological activity (Dehadrai and Bhargava, 1972) which would result in high production of oxygen.

Devassy (1983) recorded the variation in oxygen values from 1.96 to 6.28 ml/l in the Zuari and Mandovi estuaries at depths of 2 & 12 m. George (1989) observed high oxygen at the riverine stations about 5 ml/l. At the mouth the values varied from 3.11 to 4.69 ml/l in the Mandovi-Zuari estuarine system. The average oxygen concentration in both the rivers increase with distance from the river mouth (Qasim and Sen Gupta, 1981). At station M-1 it ranged from 0.95 to 5.16, at M-2 3.77 to 6.24, while Z-1 2.95 to 6.97, at Z-2 3.60 to 5.77 ml/l.

In estuaries like Narmada and Tapi in which the organic load is small, the dissolved oxygen is generally between 7-10 ml/l (Zingde et al., 1987). In the Mahanadi (Upadhyay, 1988) observed a wide range of

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variation throughout the year. High during postmonsoon about 6.05 ml/l, low during monsoon 3.65 ml/l. Sundararaj and Krishnamurthy (1975) recorded the oxygen values from 2.93 to 6.3 ml/l in the Vellar estuary.

The general tendency during all the seasons for dissolved oxygen is a gradual decrease upto station M-3 followed by increase upto station M-6. It appears that this parameter is influenced by effects of local additions depending on the location of the observation stations. during the monsoon the water movement at the sampling depths appears to be predominantly seawards resulting in high values at or near the mouth.

IV.3 pH

On average water remained alkaline at all the stations as expected. The average values of pH during each season is given in Table (3 and 4). It is seen from the tables that pH was low during the monsoon period. At the mouth, pH ranged between 7.80 and 8.01 during the premonsoon. In the Mandovi estuary, pH of the surface waters ranged from 7.55 to 7.90 whereas in the bottom waters it was from 7.53 to 7.97. Variation

TABLE - 3
Average pH values in Mandovi

	PREMONSOON	MONSOON	POSTMONSOON
<u>Surface</u>			
1) M-1	7.90	7.16	8.08
2) M-2	7.88	7.18	7.97
3) M-3	7.64	7.63	7.81
4) M-4	7.72	7.60	7.66
5) M-5	7.75	7.51	7.75
6) M-6	7.55	7.51	7.67
<u>Bottom</u>			
1) M-1	7.97	7.18	8.06
2) M-2	7.86	7.18	7.97
3) M-3	7.60	7.65	7.84
4) M-4	7.69	7.57	7.70
5) M-5	7.56	7.47	7.69
6) M-6	7.53	7.44	7.60

TABLE - 4
Average pH values in Zuari

	PREMONSOON	MONSOON	POSTMONSOON
<u>Surface</u>			
1) Z-1	7.92	7.31	8.06
2) Z-2	7.99	7.30	8.03
3) Z-3	7.91	7.47	7.86
4) Z-4	7.65	7.48	7.61
5) Z-5	7.35	7.48	7.59
6) Z-6	7.34	7.39	7.35
<u>Bottom</u>			
1) Z-1	7.94	7.30	8.09
2) Z-2	7.91	7.30	8.06
3) Z-3	7.69	7.51	7.82
4) Z-4	7.55	7.47	7.69
5) Z-5	7.28	7.42	7.50
6) Z-6	7.30	7.40	7.35

between surface and bottom waters was not significant suggesting the homogenous nature.

Lowest pH values were observed during the monsoon, the range being 7.18 to 7.63 for the surface and 7.18 to 7.65 for the bottom waters of the Mandovi estuary. During the monsoon pH was low which was due to the influence of freshwater influx and decomposition of organic matter carried by flood waters into the estuarine system (Morris et al., 1978). Rainfall, river discharge, exchange from the sea are important factors that influence pH variation in the estuarine waters. Similar trend was also observed in Zuari.

George (1989) observed high pH during premonsoon. At the mouth station pH ranged between 7.94 and 8.06 during premonsoon period. During the monsoon lowest values were observed between 7.39 to 7.74 for the Mandovi. Similar trend was observed for the Zuari.

In Narmada river estuary pH ranged from 8.3 to 8.5 in line with the pH of water of other rivers and have no relation to the tidal stage (Zingde et al., 1987).

pH ranges in the Mahanadi was high during postmonsoon about 8.48 followed by low pH in premonsoon 7-8. During monsoon pH was between 6.28 - 7.5 as reported by Upadhyay, (1988).

Ramanathan et al., (1988) observed pH values ranging from 7.9 to 8.4 in the Cauvery estuary.

In estuarine waters variations over a greater range are often observed due to several other factors such as interactions with suspended matter, influence of freshwater inputs, pollution, photosynthesis etc. The process of photosynthesis consumes carbon dioxide which in turn increases the pH of the water. The higher pH values, observed during premonsoon and post monsoon compared to monsoon, may be caused by the removal of oxygen due to high photosynthetic activity during this season. P

IV.4 PHOSPHATE

Phosphate concentration was low during the premonsoon period, but increased with the onset of

monsoon. Seasonal variation of phosphate in the surface and bottom waters were highly significant as shown in Figs. 4 & 5.

In the Mandovi estuary the phosphate concentration during the premonsoon varied from 0.53 to 1.15 $\mu\text{mol/l}$ for the surface and from 0.76 to 1.20 $\mu\text{mol/l}$ for the bottom waters. In the Zuari it ranged from 0.65 to 0.76 $\mu\text{mol/l}$ for the surface, while for the bottom waters it was 0.78 to 1.09 $\mu\text{mol/l}$. The trend of variation in the surface and bottom waters indicate a clear stratification comprising the entire estuarine system in which a surface layer of low phosphate lies over a bottom layer of high phosphate content. It is well known that nutrient concentration of the bottom water depends on the regenerative capacity of bottom sediments (Reddy and Sankaranarayanan, 1972) and there is a regular exchange of phosphorous between the sediment and overlying water (Rochford, 1951). The high concentration of phosphate observed is due to the dissolution of this nutrient from the bottom sediments. The low values recorded during the premonsoon might be due to diminished river discharge. Utilization for

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normal/l.

CONCENTRATION OF PO_4^{3-} -P (μg/l)

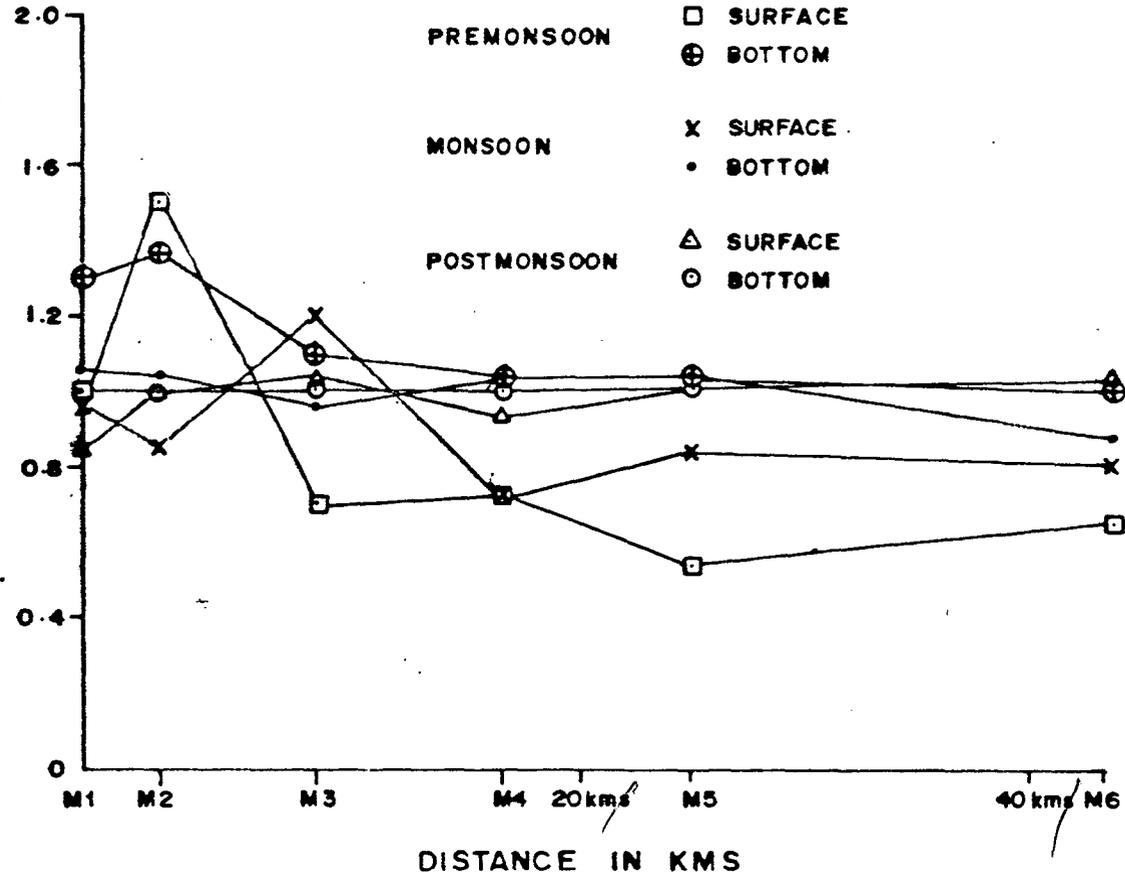


Fig.4 VARIATION OF PO_4^{3-} -P IN MANDOVI

Fig

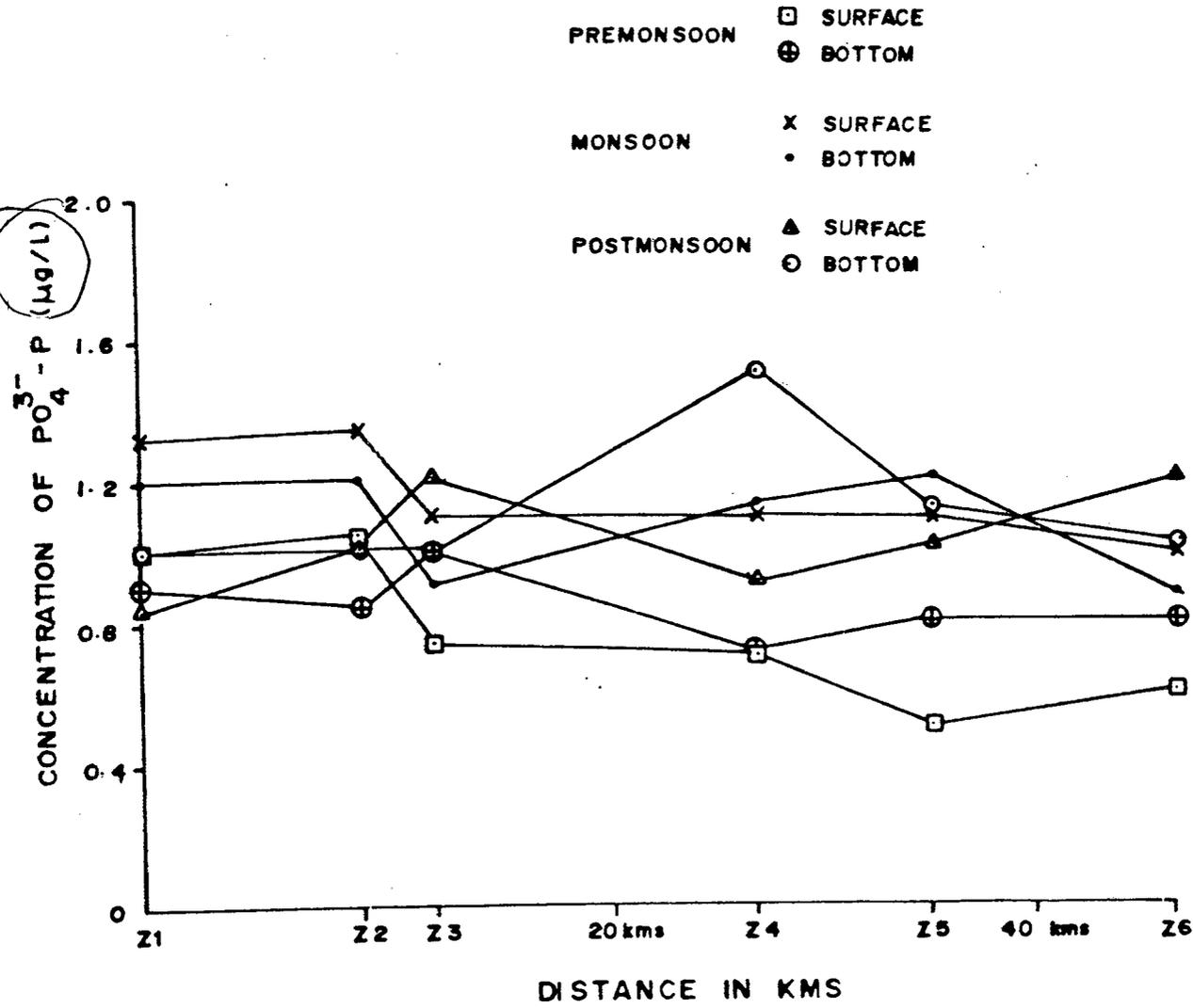


Fig.5 VARIATIONS OF $PO_4^{3-} - P$ IN ZUARI.

biological productivity would also have caused low phosphate values.

The phosphate concentration during the monsoon was high, the surface values being more than the bottom ones, along the entire estuary, which may be due to high land drainage. In the Mandovi estuary, the phosphate values varied from 1.07 to 1.36 for the surface and from 0.87 to 1.28 $\mu\text{mol/l}$ for the bottom waters. In the Zuari they were 1.77 to 2.26 $\mu\text{mol/l}$ for the surface and 1.72 to 2.04 $\mu\text{mol/l}$ for the bottom waters. One of the main sources of phosphorous in estuaries is the river runoff. During monsoon the river discharge is the highest compared to other seasons. During this period, a higher concentration of phosphorous can be expected, as observed in Bang-Pakong estuary by Windom et.al., (1988) who attributed the high concentration to release from river-borne suspended matter. High phosphate concentration could also be related to large amount of fertilizer used in agriculture during monsoon, while estuarine sediments acts as a trap for phosphate. Jitts (1959) has shown that estuarine sediments can trap 80 to

90% of phosphate when present in high levels during period of excessive runoff.

During the postmonsoon period high values of phosphate recorded suggests the possibility of intrusion of upwelled water into the estuary . In Mandovi it ranged from 0.85 to 1.27 $\mu\text{mol/l}$ for the surface and from 1.00 to 1.50 $\mu\text{mol/l}$ for the bottom waters. In Zuari it varied from 0.59 to 1.10 $\mu\text{mol/l}$ and from 0.76 to 1.23 for the surface and bottom waters respectively. The values of the bottom waters being higher than the surface waters in both the estuaries.

Does not agree with 16 graphs. More upwelling not expected in postmonsoon

The Phosphate concentrations increased towards the mouth region of both the estuaries. D'Souza (1983) also observed a similar increase towards the mouth region of the estuaries. He concluded that the high concentrations are the result of the desorption of phosphate from sediments in contact with high salinity water which was earlier adsorbed in the upper reaches of the estuary.

Earlier information on phosphate concentration in the Mandovi-Zuari estuarine system indicated a range of

0.24 - 2.6 $\mu\text{mol/l}$ during the monsoon of 1971 (Dwivedi et. al., 1974), 0.3 - 1.9 $\mu\text{mol/l}$ during monsoon of 1972 (Sankaranarayanan et. al., 1978), 0.42 - 2.5 $\mu\text{mol/l}$ during the monsoon of 1978 (Qasim and Sen Gupta, 1981). Devassy (1983) recorded a maximum phosphate concentration of 4.5 $\mu\text{mol/l}$ during postmonsoon and monsoon, and low concentration during the premonsoon.

In the Mahanadi estuary phosphate concentration was low during monsoon ranging between 0.54 and 2.40 $\mu\text{mol/l}$. Higher concentration was observed during premonsoon and postmonsoon 1.07 to 4.01 $\mu\text{mol/l}$ and 0.53 to 3.21 $\mu\text{mol/l}$ respectively as reported by Upadhyay (1988). Phosphate was significantly higher in the Cauvery estuary and does not show any regular variation. It varies from 0.12 to 0.51 $\mu\text{mol/l}$ (Ramanathan, et. al., 1988).

not high as claimed

During periods of plankton bloom large amounts of phosphate are removed from the water column. The productivity in these two estuaries have been reported to show two peaks one during premonsoon and the other during postmonsoon (Dehadrai and Bhargava, 1972). This high productivity is followed by oxidation of organic

nutrients

^{handwritten} matter produced which will enhance the ^{abundance} dissolution of some elements (Martin and Whitefield, 1981). In the Mandovi-Zuari estuarine system occurrence of Trichodesmium blooms (a blue green algae) have been reported (Devassy, 1978, 1979). The subsequent decay of the bloom may liberate trace elements from organic matter. One of the reasons for the increase in phosphate concentration towards high salinity region during premonsoon and postmonsoon may be due to the decay of this organic matter and subsequent release of the elements. High phosphate concentration have been reported during decay of Trichodesmium (Devassy et al., 1978).

IV.5 SILICATE

There is a general increase in the concentration from the mouth of the estuary to upstream. In the upper reaches of the estuary due to the salinity influence, the concentration is comparatively uniform throughout the year. Fig. (6 & 7) show the seasonal variation of silicate in Mandovi and Zuari estuaries.

CA

Normal ?

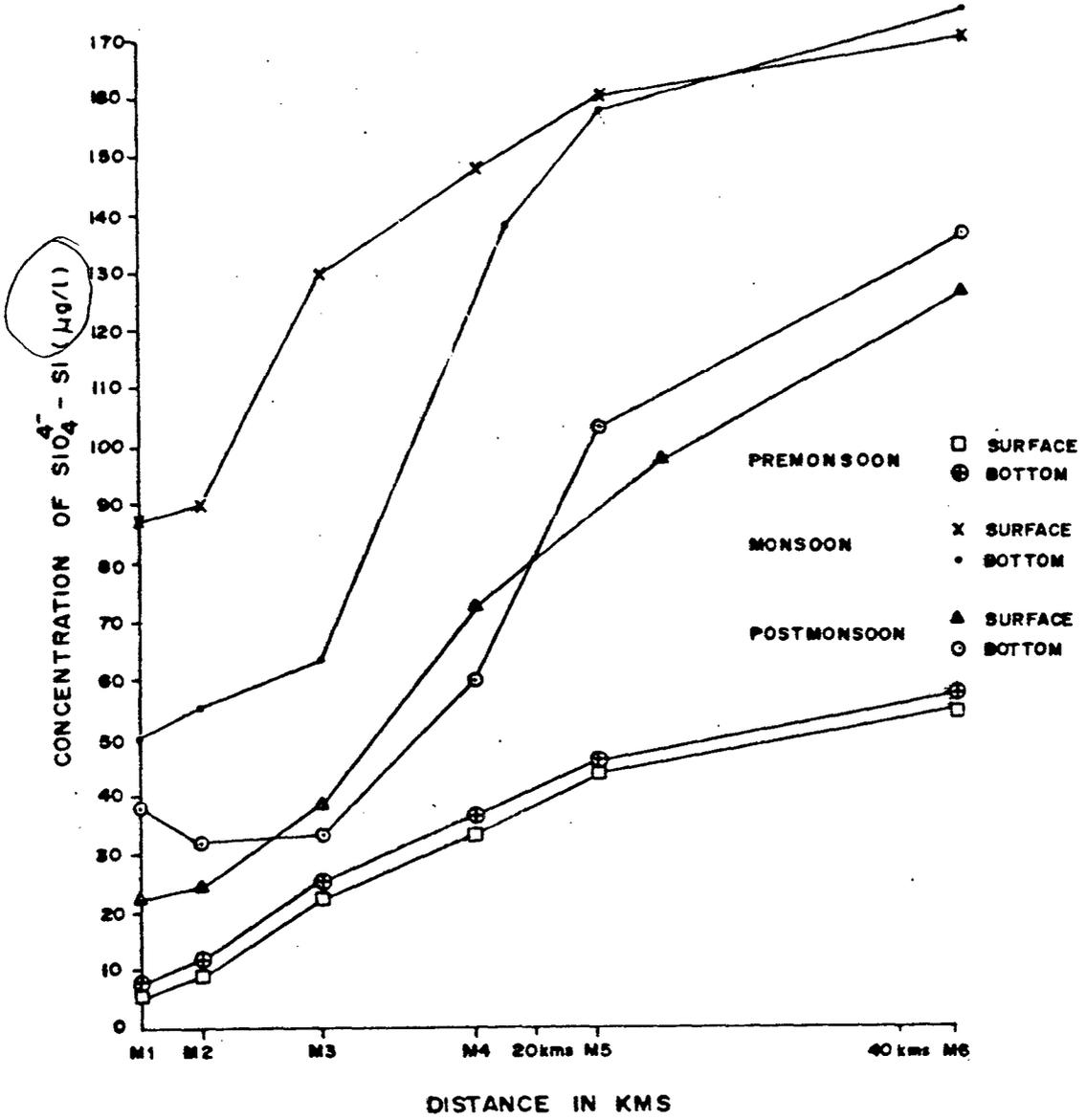


Fig 6 VARIATION OF $\text{SiO}_4^{4-} - \text{Si}$ IN MONDOVI

CT

sample?

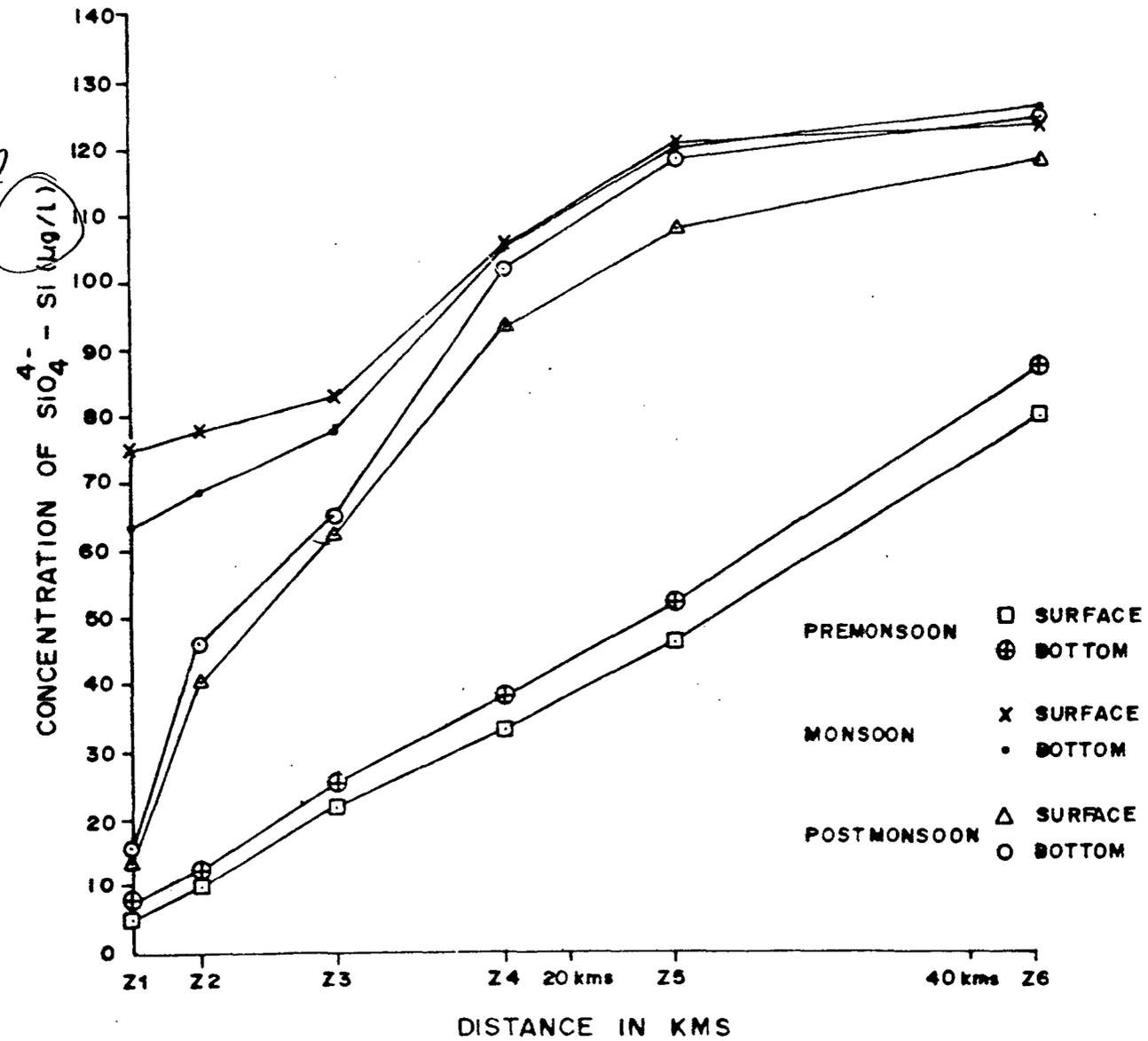


Fig.7 VARIATION OF $\text{SiO}_4^{4-} - \text{Si}$ IN ZUARI

During the premonsoon silicate varied from 6.79 to 54.04 $\mu\text{mol/l}$ for the surface waters, while it was from 7.24 to 57.14 $\mu\text{mol/l}$ for the bottom waters of the Mandovi. In the Zuari similar variations were from 5.62 to 80.63 and 8.44 to 89.09 $\mu\text{mol/l}$ for the surface and bottom waters respectively, the values of the bottom waters being higher than the surface waters of both the estuaries. This silicate distribution appears to be largely governed by the river water discharge. Maximum concentration of silicate occurs during south west monsoon when the river discharge is maximum, but during the premonsoon when the river discharge is minimum the variation and concentration of silicate are minimum.

Silicate concentration was the highest during the monsoon. In Mandovi, the concentration varied from 89.35 to 168.99 $\mu\text{mol/l}$ for the surface waters, while it varied from 49.98 to 175.12 $\mu\text{mol/l}$ for the bottom waters. In Zuari it varied between 75.09 and 124.83 for the surface and from 63.69 $\mu\text{mol/l}$ to 126.00 $\mu\text{mol/l}$ for the bottom waters. In both the estuaries, the concentration decreased downstream. Distribution of silicate showed a high concentration at the river end

which decreased gradually downstream with low silicate values at the sea end in conformity with the pattern found in most of the estuaries.

Distribution of silicate during postmonsoon showed a regular pattern i.e. high concentration at the river end which decreased gradually downstream. Silicate is mainly supplied by the river water and there is almost always a settlement at the confluence of the river and the sea. In Mandovi it ranged between 22.13 and 126.40 $\mu\text{mol/l}$ for the surface waters and between 38.92 and 137.31 $\mu\text{mol/l}$ for the bottom waters. While in Zuari it varied between 14.18 and 119.01 $\mu\text{mol/l}$ for the surface and from 16.52 to 125.34 for the bottom waters.

During this season the range in silicate concentration was narrow, though the station at the river end had comparatively higher concentration than the stations at the sea end.

This is in agreement with the observation of De Souza (1981) who recorded a silicate concentration from 10 and 70 $\mu\text{mol/l}$ in the Mandovi and from 10 and 50 $\mu\text{mol/l}$ in Zuari during the premonsoon. During the

monsoon the concentration varied between 100 and 160 $\mu\text{mol/l}$, while in Zuari it varied from 10 to 190 $\mu\text{mol/l}$. During the postmonsoon it ranged from 10 to 80 $\mu\text{mol/l}$ in Mandovi and from 10 to 60 $\mu\text{mol/l}$ in Zuari. George (1989) observed high concentration of silicate during all seasons at the upper reaches of the Mandovi-Zuari estuaries. During postmonsoon and premonsoon the concentration at the riverine end varied from 47.79 to 74.8 $\mu\text{mol/l}$, while at the lower reaches it varied from 4.59 to 9.07 $\mu\text{mol/l}$. During monsoon high concentrations were observed throughout the river. The values ranged from 112.3 to 152.9 $\mu\text{mol/l}$.

Qasim and Sen Gupta (1981) recorded silicate range from 3 to 210 $\mu\text{mol/l}$ in the Mandovi and from 3 to 196 $\mu\text{mol/l}$ in the Zuari. Silicate concentrations were lower in the estuarine region than upstream.

Estuarine profiles of silicate in Mahanadi showed high concentration at the river end which decreased gradually downstream with low values at the sea end and is in conformity with the pattern found in most of the estuaries (Upadhaya, 1988).

Silicates are concentrated more in the upper reaches and this is to be expected as it is of land origin; whereas in the outer reaches the concentration are more or less similar to those in seawater. Both Mandovi and Zuari rivers are surrounded by hilly terrain with dense vegetation, consequently the laterite soils of these forests is rich in humus which is associated with silicates.

What is the relation with salinity?

CHAPTER – V

DISTRIBUTION AND BEHAVIOUR OF ARSENIC SPECIES IN THE ESTUARINE SYSTEM

V. DISTRIBUTION AND BEHAVIOUR OF ARSENIC SPECIES IN THE ESTUARINE SYSTEM

V.1 ARSENATE

Rivers transport trace metals and metalloids to the oceans in dissolved, colloidal and particulate forms. In estuaries where river water and coastal water of different compositions are mixed, strong gradients in chemical and physico-chemical properties occur (Dyer, 1972; Phillips 1972; Burton, 1976). As a result drastic changes in the behaviour of these can take place in an estuary.

Information on the behaviour of arsenic in estuarine waters is at present limited. The dominant form of arsenic in both saline and fresh water regions is inorganic arsenic i.e. arsenate. In the estuarine waters of the Mandovi and Zuari arsenate was found to be the dominant species. This is consistent with the thermodynamic considerations that arsenate is a more stable form than other species of this element (Sillen, 1961). Arsenate concentrations in the Mandovi estuary during premonsoon varied from 0.11 to 0.22 $\mu\text{g/l}$ in the

surface waters, while the same was from 0.13 $\mu\text{g}/\text{l}$ to 0.27 $\mu\text{g}/\text{l}$ in the bottom waters. Arsenate concentration in the Zuari estuary varied from 0.13 to 0.20 $\mu\text{g}/\text{l}$ in the surface waters and from 0.18 to 0.24 $\mu\text{g}/\text{l}$ for the bottom waters respectively for the same period. It was found that the bottom values of arsenate at a few stations were higher than those of the surface waters. Higher concentration of arsenate over arsenite is in conformity with the well oxygenated conditions of the waters (higher redox potential) coupled with catalytic activity of the oxidizing organisms. It is observed that dissolved oxygen varied from 3.73 ml/l to 4.45 ml/l for the surface waters, and from 3.58 to 4.16 ml/l for the bottom waters in the Mandovi estuary. The surface and bottom waters were well oxygenated at all the stations in both the estuaries. The concentrations of arsenate and 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 fresh water zone, with a maximum in the mid-estuarine region. One of the factors which may 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). In marine waters diatoms are the dominant forms of phytoplankton organisms in these two estuaries, production at the Mandovi mouth being higher than that at the Zuari mouth (Devassy, 1983). The high concentration of arsenate observed at the mouth of the two rivers can be due to the above reasons. During the pre-monsoon the bottom values of arsenate was high at Z-1 to Z-3, with a minimum at Z-5, while the surface values exhibited a maximum only at Z-3. All the other stations had a low constant value throughout. Generally high values are observed at the marine as well as at the fresh water ends. In Mandovi bottom concentrations decreased from M-6 to M-5. In the mid-estuary the concentration was very low with another high concentration at M-2.

*In what way
diatoms affect
As concentration?*

Arsenate, during the monsoon period, was the highest as compared to other seasons of the year. During the monsoon the surface values ranged from 0.40 to 0.78 $\mu\text{g}/\text{l}$, and from 0.34 to 0.79 $\mu\text{g}/\text{l}$ for the bottom

waters of the Mandovi estuary. In Zuari it ranged from 0.45 to 0.79 $\mu\text{g}/\text{l}$ at the surface and from 0.42 to 0.78 $\mu\text{g}/\text{l}$ at the bottom, surface values being higher than the bottom values in both the estuaries. The bottom values were high at the mouth of the estuary, but the concentration of arsenate was the highest upstream, which appears to be the effect of land drainage. Large variations observed at various stations 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 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. Higher concentration of arsenate during the monsoon period in the estuaries as compared to the other seasons confirm that much of the arsenate is of land origin. Higher concentration in the bottom water suggests active recycling of the element.

During monsoon, the period of maximum precipitation and river discharge, the concentration of arsenate was the maximum. Rain water analysis revealed significant

amount of arsenate, whereas arsenite was not detected in any of the samples analysed. The concentration of arsenate was very low about 0.02 and 0.03 $\mu\text{g/l}$ respectively. Goa receives on an average 261 cm of rainfall every year. Of this 90% is during June to September. Shipping and mining activities are known to contribute trace metals and other pollutants to the environment (Abdulla et al., 1972; Valenta et al., 1983). These factors could have kept the concentration of arsenate at an elevated level during the monsoon. Disturbances of bottom sediment could be one of the major reasons for the high concentration in the water column during monsoon in both the estuaries. Large quantities of iron ore are mined and transported through these estuaries, and there is a possibility of some arsenic associated with iron as FeAsS , leaching into the river. The high concentration of arsenate could be due to the drainage from mines which proliferate in the upper reaches of the estuary and dissolution from river-borne sediments. Contributions from these sources coupled with the high and frequently mixed turbidity are believed to explain the variations in arsenate concentration found in these estuaries. Knox et al.,

o
what are
its levels in
rainwater
elsewhere?

(1984) have suggested that turbidity maximum may affect the dissolved arsenic speciation by oxidation of arsenic (III) to arsenic (V) and have implicated manganese in this process.

In view of strong adsorptive affinity of arsenite and arsenate for hydrous iron oxide (Pierce and Moore; 1982) and the preponderance of iron-arsenic ores such as arsenopyrite, it is not surprising to find arsenic associated with iron in the aquatic environment (Neal et al., 1979; Langston, 1980). The concentration of arsenic in two iron ore samples analysed were 50.44 $\mu\text{g/g}$ and 48.93 $\mu\text{g/g}$ respectively and hence the 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 M-6 and Z-6 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 can be seen decreasing seaward. About 70% of the iron ore is mined from north Goa and is loaded between stations M-5 and M-6 and the remaining 30% from South Goa near stations Z-5 and Z-6 where high concentrations of arsenate are

observed. Mandovi handles more iron ore while Zuari comparatively less. Hence the high concentration of arsenate at station M-6 could be mainly due to this reason while in Zuari, the arsenate concentration is low, which is higher than the stations at the marine end.

The high concentration of arsenate must be the result of remobilization 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, Aron and involve arsenic diffusion from pore waters (Carpenter et al., 1978, Langston, 1983; Knox et al.; 1984) or desorption from suspended matter (Howard et al., 1984; Seyler, 1985). The salinity decrease along the salinity gradient may indicate a preferential settling of the coarse grained fraction near the river mouth. | how ?

The most notable feature of arsenate concentration variation over the year is the low values observed during the months January to April, followed by an

elevated level during the monsoon (June to September). Low values were observed again for the months October to May. A similar pattern was also observed for other elements like iron, suggesting that trace element concentrations are partially regulated by seasonal climatic conditions. Beck et al., (1974) points out that metals are flushed out at high concentrations following rains. Hence river discharge which is directly related to rainfall, where the river stage is not artificially controlled, should be related to trace element concentrations. Waslenchuk (1979) reveals that rivers with drainage basins primarily in the crystalline igneous and metamorphic terrain have low arsenic concentrations than those having drainage basins restricted to the sedimentary terrain.

-3

Further down the estuary in the $15 - 30 \times 10^3$ salinity region the arsenate levels were remarkably stable. Near the marine-end, where arsenate concentrations of less than $0.05 \mu\text{g/l}$ are to be anticipated, presence of elevated levels can be explained only by a significant input in this region. Releases from river-borne sediments are an additional

source of arsenic. The bottom waters had higher concentrations of arsenate than the surface waters (Fig 8, 9 & 10) of both the estuaries. In river and estuarine waters arsenate is complexed by low molecular weight dissolved organic matter (Waslenchuk and Windom, 1978). Complexation apparently affects conservative behaviour of arsenic in the estuary by preventing interaction with active, solid phase, organic and inorganic material. Complexation may, also, play a similar role in fresh water. Dissolved organic matter might partially control the concentration of dissolved arsenic. It is known that riverine concentrations are controlled in part by rain water dilutions.

In the water column the increase in ionic strength occurring at the fresh water-sea water interface enhances the desorption processes through competition between major seawater cations for the adsorption sites on suspended matter and/or through a decrease in the electrical charge on the surface of particulates. From deposited sediments arsenic is mobilized, probably following the dissolution of hydrous Fe and Mn oxides causing elevated arsenic concentration in the water

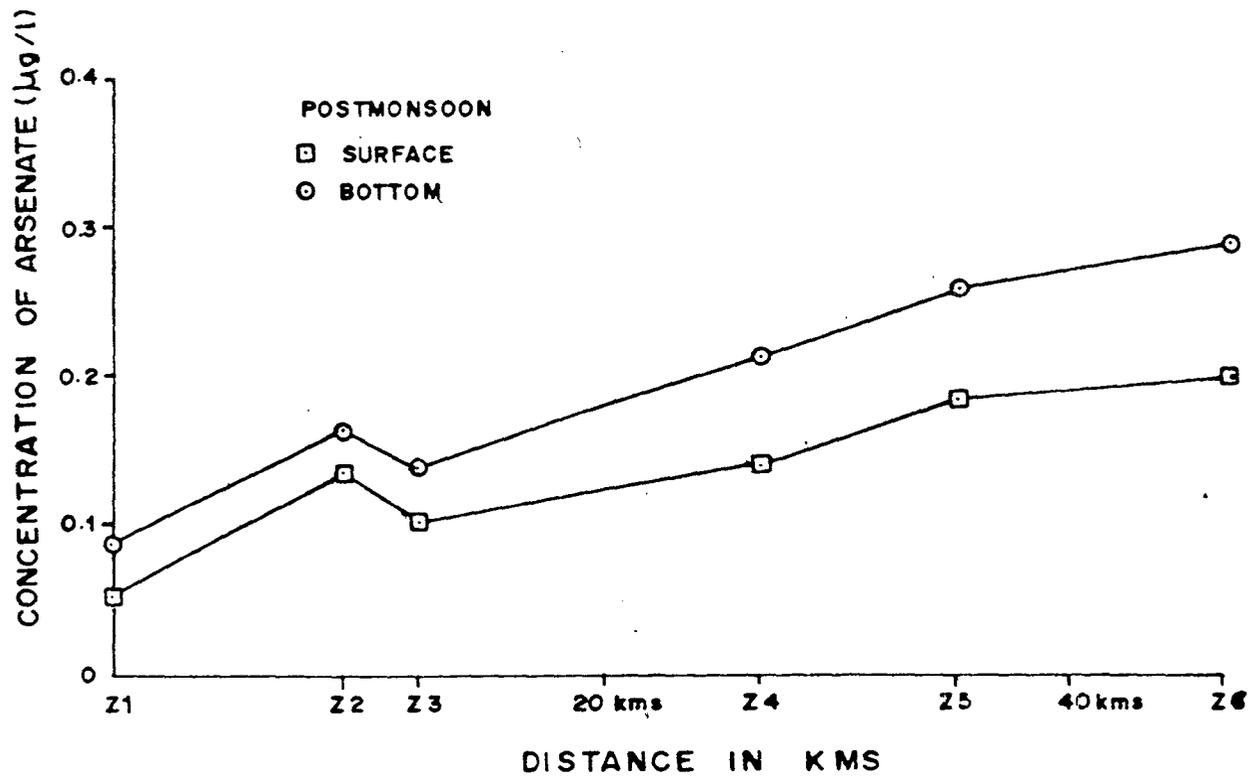


Fig.8 VARIATIONS IN THE CONCENTRATION OF ARSENATE IN ZUARI

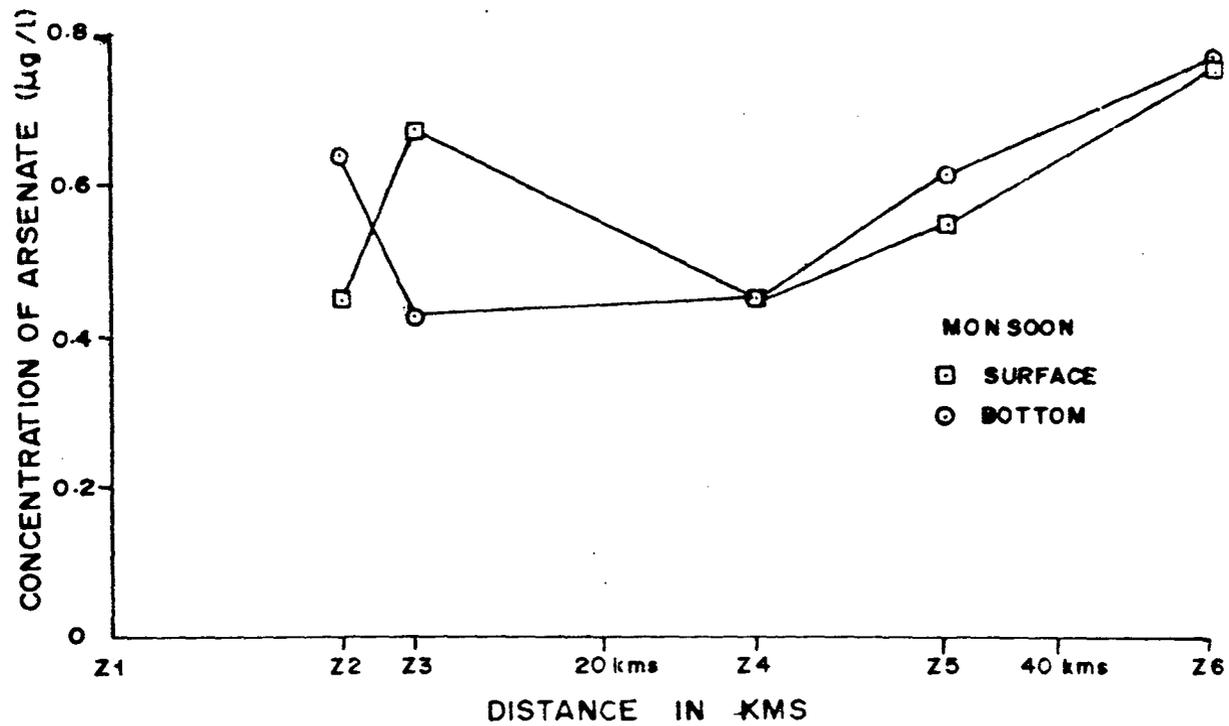


Fig. 9 VARIATIONS IN THE CONCENTRATION OF ARSENATE IN ZUARI

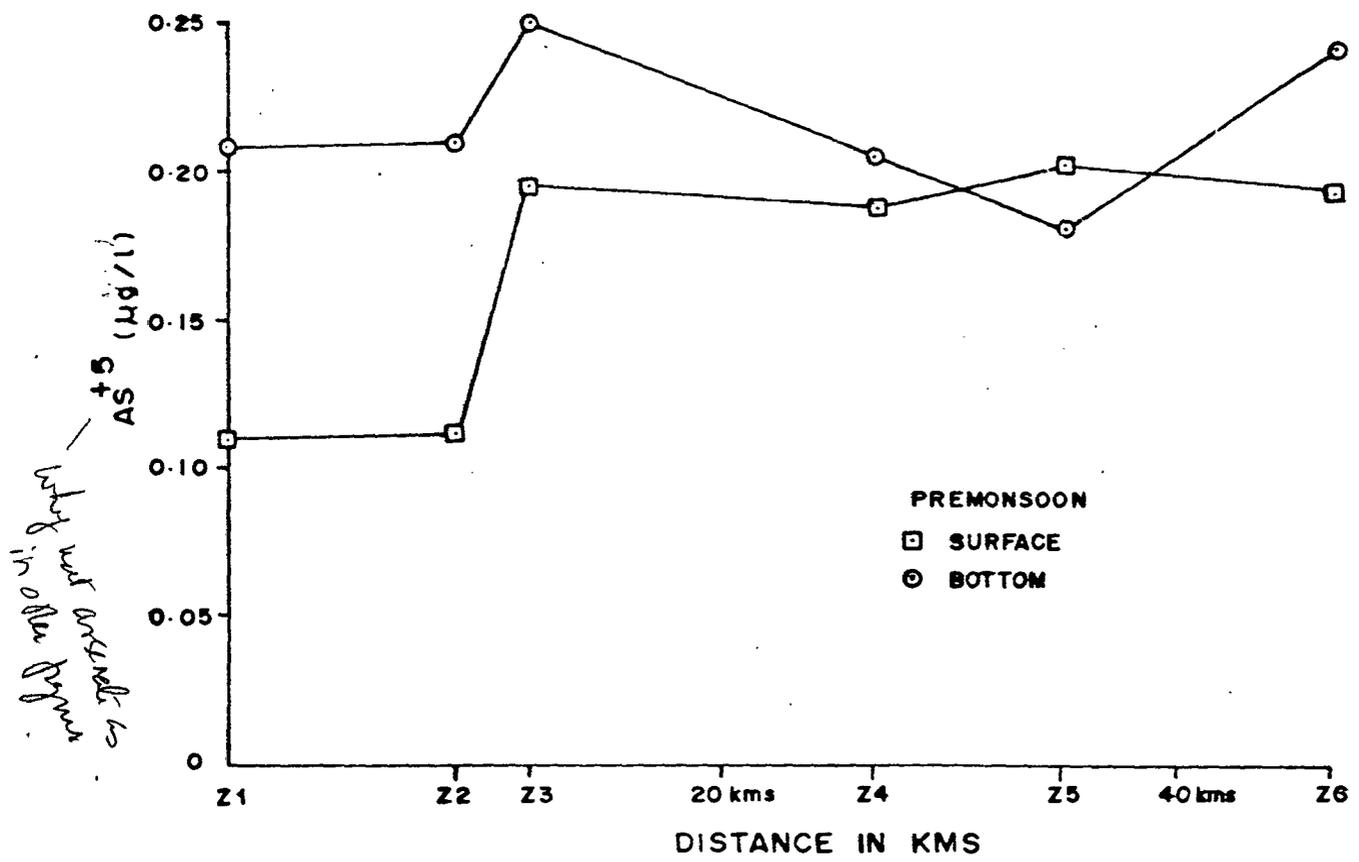


Fig.10 VARIATIONS IN THE CONCENTRATION OF AS⁺⁵ IN ZUARI

column. The observation of a maximum in mid estuarine waters indicate that reducing conditions prevail in the sediment (Elbaz-Poulichet et al., 1990b). During the monsoons the sediments are resuspended leading to a release of arsenic to the water column, hence a high concentration of arsenate is observed in both the estuaries. During monsoon a salt wedge upto 10 kms upstream in Mandovi and 12 kms upstream in Zuari has been reported by Qasim and Sen Gupta (1981), while during other seasons the water column remains well mixed. The relationship between the ions present in the water column and adsorbed metal ions is well established.

The salt wedge resulting in a steep salinity gradient at mid-depth minimizes mixing between surface fresh water and the underlying salt water. Hence the salinity measured here at mid depth during monsoon may not be representative of the salinity of water overlying the sediment surface, which is actually responsible for the exchange process. The reason for any increase in arsenate at M-2 after the minimum at M-3 during monsoon could possibly be due to a possible reducing condition

prevailing at the sediment water interface, caused by stratification resulting in the poor vertical exchange because of the salt wedge. The steep salinity gradient at mid depth minimizes mixing between surface fresh water and the underlying salt water, which creates a natural barrier against the downward advection of dissolved oxygen. Hence the bottom water and sediments become oxygen depleted due to organic matter decomposition. Metals like arsenic are released into the overlying waters due to the low redox potential. This has been observed by Keeney-Kennicut and Presley, (1986) in Brazos river which is a salt wedge type estuary. This may be a reason for the high values of arsenate during the monsoon.

Surface and bottom DO is similar in this situation (p. 48). Hence statement is incorrect.

During the post monsoon arsenate varied from 0.08 to 0.17 $\mu\text{g}/\text{l}$ for the surface waters, and from 0.12 to 0.30 $\mu\text{g}/\text{l}$ for the bottom waters of Mandovi estuary. In the Zuari estuary it varied from 0.05 to 0.20 $\mu\text{g}/\text{l}$ for the surface waters, and from 0.09 to 0.29 $\mu\text{g}/\text{l}$ for the bottom waters. The concentrations of arsenate is higher in the bottom waters than the surface waters in the Mandovi, while in Zuari at Z-1 the surface value being

higher than the bottom waters, whereafter a steady decrease takes place (Fig.11-13). Once again the bottom values are higher from stations Z-2 to Z-6. Post monsoon values were more or less similar to the concentrations during the premonsoon. Eventhough there was a variable but steady increase towards the upper reaches, both the surface and bottom values at station Z-2 exhibited a maximum in Zuari, while a maximum was observed at M-3 in Mandovi during the same period. These types of sudden changes may be due to the dynamic nature of the estuaries or even due to the influence of certain local disturbances. From a high bottom concentration at Z-6 it gradually slopes to a minimum at Z-3 and a sharp increase is again observed at Z-2, followed by a drop at Z-1. According to Devassy (1983), Mandovi retains typical estuarine conditions most part of the year, with high phytoplankton counts, Chlorophyll a concentration and benthic production; while in Zuari the influence of sea is more and subsequently production is less. In Mandovi plankton analysis revealed a significantly high level of arsenate, the concentration being higher at the mouth of the estuary (22.37 $\mu\text{g/g}$) while at the upper reaches it decreased gradually. At

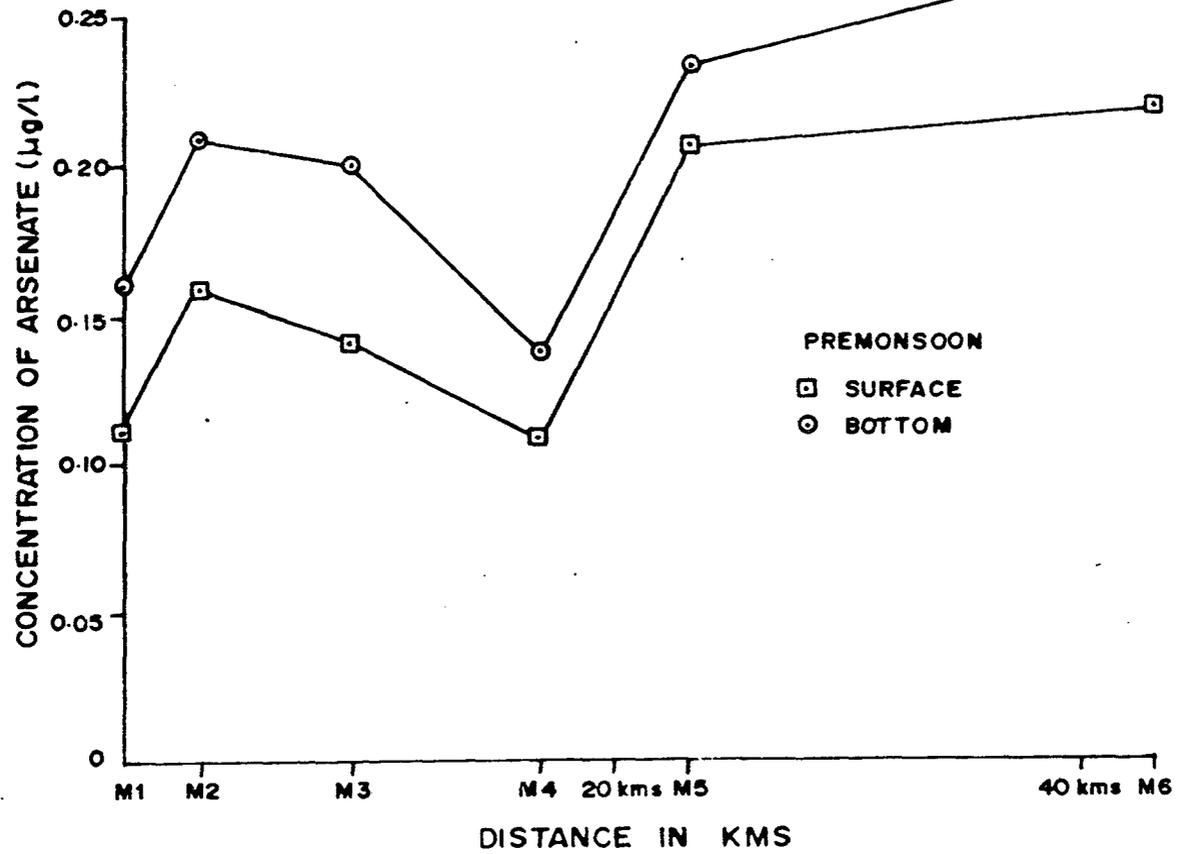


Fig.11 VARIATIONS IN THE CONCENTRATION OF ARSENATE IN MANDOVI

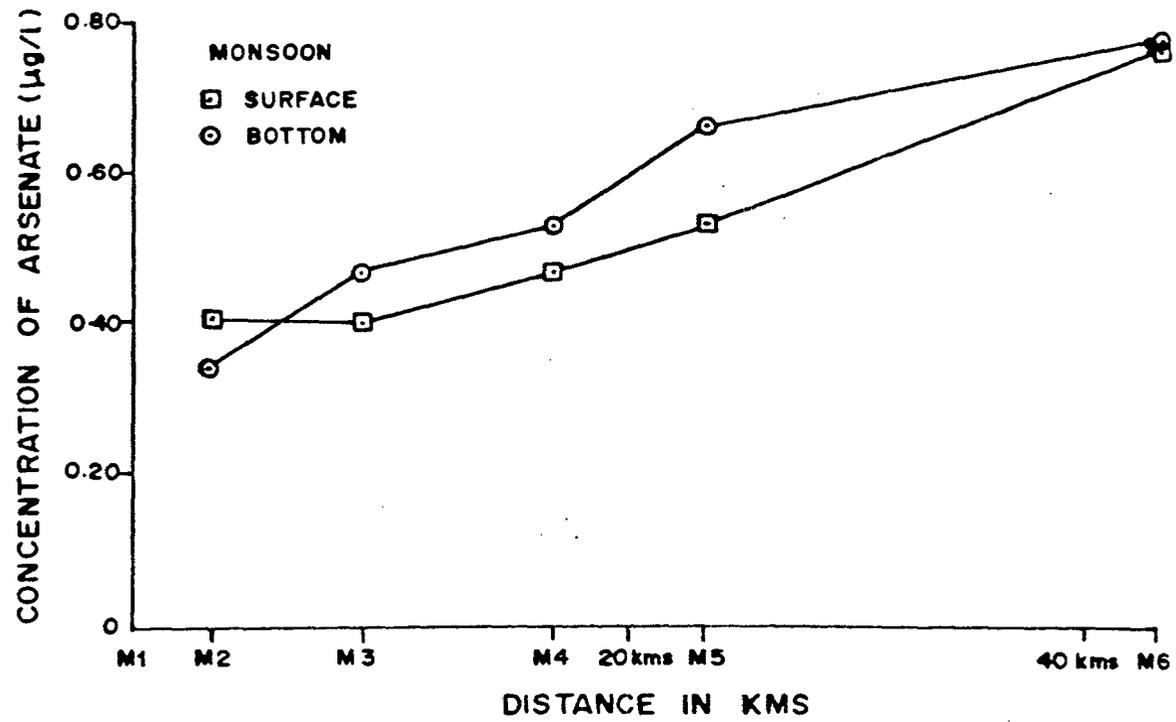


Fig.12 VARIATIONS OF THE CONCENTRATION OF ARSENATE IN MANDOVI.

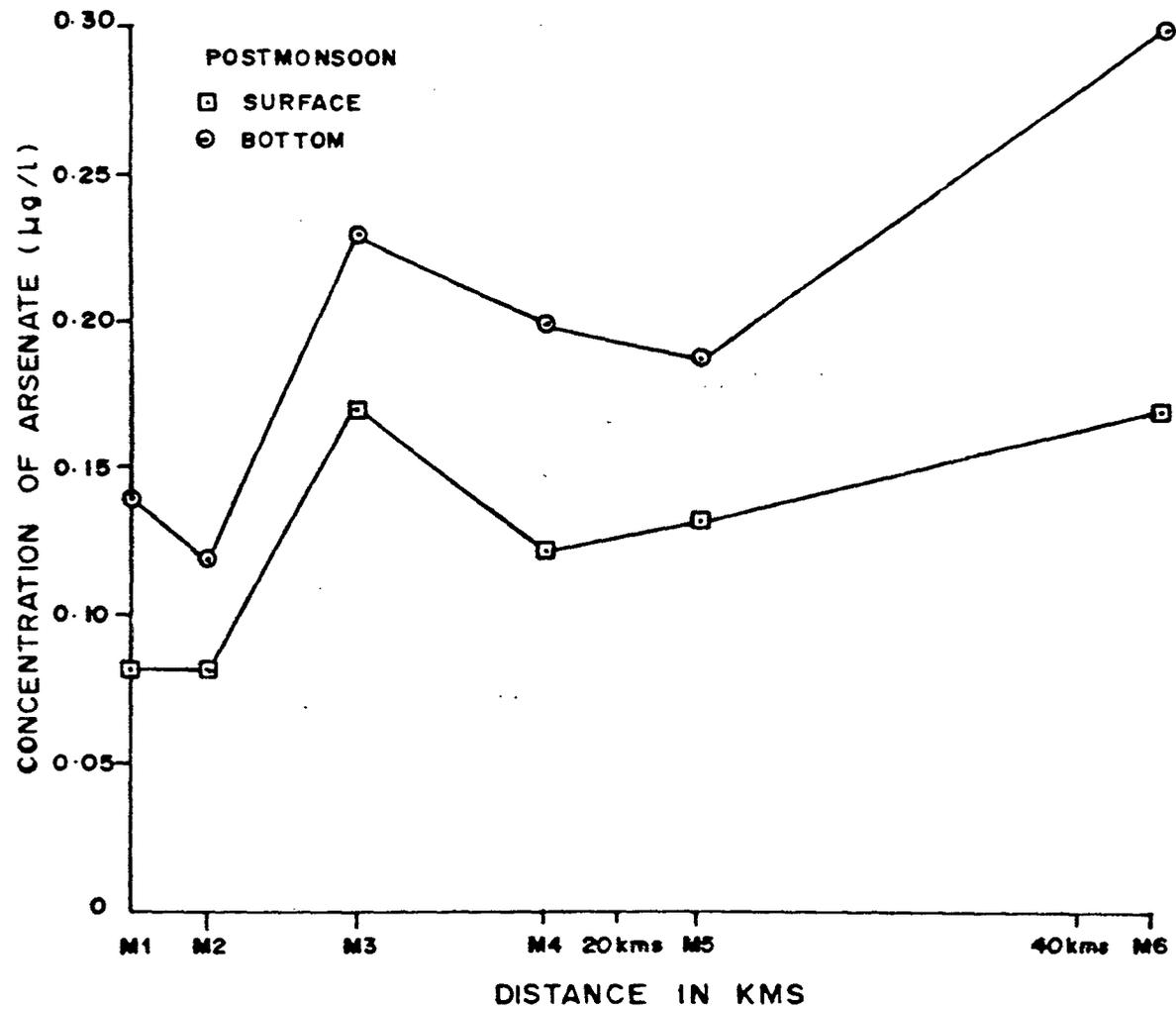


Fig.13 VARIATIONS IN THE CONCENTRATION OF ARSENATE IN MANDOVI

station M-6 it was about 18.44 $\mu\text{g/g}$ (dry weight). The values obtained were comparable with those reported by Leatherland et al. (1973) who found 14.5 $\mu\text{g/g}$ in a copepod and 42 $\mu\text{g/g}$ in euphausid from the northeast Atlantic. Kennedy (1976) reported values from Newfoundland ranging between 0.9 and 8.9 $\mu\text{g/g}$. Zooplankton derives arsenic through phytoplankton which is known to extract this element as a nutrient having a biological function in seawater as a phosphate analogue (Johnson, 1972). Zooplankton forms an important link in the food chain mediating the incorporation of this metalloid to higher trophic levels. Onishi (1969) reported the general concentration levels of arsenic in marine animals (mostly fishes and other higher organisms) as between 0.1 and 50 $\mu\text{g/g}$. Zooplankton may also be responsible in contributing this element to the sediments on decaying. The concentration of arsenic was less at M-2 (9.45 $\mu\text{g/g}$). Hence the high values in Mandovi may be due to high plankton or benthic production which solubilize metals. Another fact is that Panjim sewage outlet joins the river Mandovi somewhere before station M-2. The sewage brings in

plenty of organic load and metals associated with it. The sewage from the Mandovi showed a concentration of 0.23 $\mu\text{g}/\text{l}$ of arsenate and 0.08 $\mu\text{g}/\text{l}$ of arsenite respectively; while that from the Zuari contains lower levels of arsenate and arsenite about 0.08 and 0.03 $\mu\text{g}/\text{l}$ respectively. This explains the high values of arsenate observed in Mandovi.

V.2. ARSENITE

Significant amounts of arsenite are present in the estuarine waters of both Mandovi and Zuari. It was observed that arsenite exhibited a maximum at stations where arsenate was low in concentrations and vice versa. The presence of arsenite in the estuaries suggest 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.

During the premonsoon, arsenite was found in very low concentration in surface and bottom waters. Average values of arsenite during the three seasons are given in

(Tables 7 & 8). Arsenite concentrations varied from undetectable levels to 0.07 $\mu\text{g}/\text{l}$ for the surface waters, and from undetectable levels to 0.10 $\mu\text{g}/\text{l}$ for the bottom waters of the Mandovi. While it varied from 0.04 to 0.11 $\mu\text{g}/\text{l}$ for the surface waters and from 0.07 to 0.16 $\mu\text{g}/\text{l}$ for the bottom water of the Zuari. Surface and bottom waters of the Mandovi did not show any significant variations at most of the stations except at M-2 and M-6. Arsenite exhibited two small peaks, one at M-2 near the mouth of the estuary and one at M-6. While at M-5 there is a drop in concentration both at the surface and at the bottom. In Zuari too, a peak was observed at the mouth of the Zuari (Z-2) while at Z-5 there is a drop in the surface concentration, and an elevated bottom concentration. Both surface and bottom values were low at Z-6. Productivity is generally high during premonsoon and occasional Trichodesmium blooms occur at the mouth of the estuary. In unpolluted natural waters the occurrence of arsenite seems to be closely linked to primary productivity. During periods of high biological activity arsenate (V) is taken up readily by planktonic algae whereas arsenite As(III) is released in the surrounding media (Andreae, 1978;

TABLE - 7

Average values of arsenite in Mandovi ($\mu\text{g/l}$)

		PREMONSOON	MONSOON	POSTMONSOON
<u>Surface</u>				
1)	M-1	0.05	0.08	0.04
2)	M-2	0.04	0.09	0.07
3)	M-3	0.07	0.07	0.15
4)	M-4	0.06	0.17	0.06
5)	M-5	0.00	0.12	0.09
6)	M-6	0.05	0.14	0.07
<u>Bottom</u>				
1)	M-1	0.03	0.07	0.05
2)	M-2	0.10	0.07	0.09
3)	M-3	0.07	0.13	0.18
4)	M-4	0.07	0.06	0.11
5)	M-5	0.00	0.08	0.10
6)	M-6	0.07	0.12	0.09

TABLE - 8

Average values of arsenite in Zuari ($\mu\text{g/l}$)

	PREMONSOON	MONSOON	POSTMONSOON
<u>Surface</u>			
1) Z-1	0.07	0.18	0.02
2) Z-2	0.11	0.17	0.04
3) Z-3	0.09	0.16	0.04
4) Z-4	0.10	0.06	0.06
5) Z-5	0.05	0.19	0.05
6) Z-6	0.04	0.15	0.14
<u>Bottom</u>			
1) Z-1	0.07	0.18	0.03
2) Z-2	0.16	0.16	0.04
3) Z-3	0.09	0.11	0.07
4) Z-4	0.07	0.09	0.09
5) Z-5	0.13	0.14	0.07
6) Z-6	0.08	0.13	0.04

Johnson and Burke, 1978). In addition to participating in biological processes, arsenite might eventually be produced by the oxidation of organo--arsenicals including methylated species, but these compounds are known to be chemically very stable and difficult to oxidize in natural conditions (Sanders, 1985; Froelich et al., 1985). Hence the high values of arsenite at the mouth of the estuary is dependent on the phytoplankton population. Diatoms generally dominated the phytoplankton population. The predominant forms were Chaetoceros, Navicula, Nitzschia, Skeletonema, Rhizosolenia and Leptocylindrus (Devassy, 1983). Chlorophyll a concentration was found to be high in the Mandovi and Zuari estuarine system (Devassy, 1983). The presence of phytoplankton community may play an active role in producing arsenite and methylated arsenic compounds. In addition decaying Trichodesmium are known to release trace metals into the water column. Arsenate, the primary inorganic form of arsenic in oxidised natural waters, is highly reactive in productive estuaries, actively taken up by phytoplankton, transformed into reduced and methylated

forms and released back into the water column. The degree of arsenic methylation that takes place is proportional to the rate of primary production, and the chemical form of arsenic produced is dependent on the species of phytoplankton present. The various chemical forms of arsenic differ in their stability, reactivity and toxicity, thus the observed variations have considerable geochemical and ecological significance. Algal incorporation of arsenic and subsequent transformation of chemical forms leads to an increase in reduced and methylated arsenicals which are less available to phytoplankton, but are much more toxic to higher organisms (Sanders, 1985). Howard et al (1982) noted that the bioreduction of arsenate in the river Beaulieu (UK) is controlled by seasonal variation of the phytoplankton population, which in turn are dependent on surface water temperature, ambient light levels and nutrient availability. In the Zuari estuary, bottom values were higher than the surface values at most of the stations. The bottom sediments are disturbed by dredging, currents, barge traffic etc. which bring the trace metals into the overlying water column. During the premonsoon the renewal time of the water in the

Mandovi is about 50 days(Qasim and Sen Gupta, 1981) and hence release of metals from bottom sediments must also be significant. High temperature is observed during this period (premonsoon) (George, 1989). High temperature favours decomposition (Boyle et al; 1981). The decomposition of organic matter sets free trace metals in the sediments which can be resuspended by tides and dredging (Martin and Whitfield, 1983). De Groot (1976) found that dredging increased the concentration of trace metals in Rottardam Harbour. Periodic dredging is carried out at the mouth of the Zuari which could add trace metals into the overlying water.

There is no particular trend of variation for the concentration of arsenite during the monsoon. The values varied from 0.07 to 0.17 $\mu\text{g/l}$ for the surface water and from 0.06 to 0.13 $\mu\text{g/l}$ for the bottom waters of the Mandovi. The arsenite values for Zuari varied from 0.06 to 0.19 $\mu\text{g/l}$ for the surface, from 0.09 to 0.16 $\mu\text{g/l}$ for the the bottom respectively. The surface values being higher than the bottom waters of both the estuaries. In Mandovi at the mouth of the estuary (M-2)

the surface values were high and bottom values were low. The surface concentration drops at M-3 and it again increases at M-4 and gradually drops towards the freshwater region. At the freshwater region both the surface and bottom values were more or less of the same magnitude. Rapid reduction of arsenate must be producing arsenite at the mouth of the estuary. The amount of arsenic in reduced form is related to phytoplankton i.e. the productivity of the estuaries. In Zuari, the trend was also similar to the high values at the mouth of the estuary (Z-2) both surface and bottom values exhibiting a peak only at Z-5. During the monsoon the surface values are higher than the bottom values at most of the stations. The magnitude of the arsenite values being low compared to the values obtained during the other seasons. During monsoon the transport of the ores and shipping activities are much reduced and hence the contributions from these sources are less. It could be seen that during the monsoon when the highest water discharge occurred, low concentration of arsenite were observed, whereas during the low

discharge i.e. premonsoon, highest concentration of arsenite were observed.

Studies on arsenic speciation in anoxic system had suggested that not all arsenic was reduced to arsenite even under highly reducing conditions (Andreae, 1979 ; Andreae & Froelich, 1984). Highest fraction of As (III) reported was found in anoxic waters of Saanich Inlet, British Columbia, where 80% of inorganic arsenic was present as arsenite (Peterson & Carpenter, 1983). High proportion of arsenite was observed in the Chesapeake Bay during summer, which may not be caused by biological reduction alone. A large portion of the Bay is anoxic during summer, with anoxic building in bottom waters during April-May as stratification increases, then largely disappearing in late October-November (Officer et al 1984). Thus subsurface flows of sea water can cause oxygen depletion in estuaries, setting up conditions that are conducive to chemical reduction before sub surface water mixes with river water. In the Zuari too both the surface and bottom values showed a peak. The river discharge during this period is much higher compared to other seasons. Shipping and mining

activities are known to contribute trace metals into the environment (Abdullah et al 1972 ; Valenta et al 1983). These factors could have enhanced the concentration of arsenite during the monsoon as was indicated earlier from analysis of arsenic in iron ores. Periodic dredging at the mouth of the estuary is carried out by the Port authorities which could bring trace metals back to the water column.

Algae vary considerably in their response to arsenic. Not all algae are able to transform arsenic nor do they produce and release the same compounds (Andreae, 1978 ; Andreae & Klumpp, 1979 ; Sanders and Windom, 1980; Sanders, 1983 ; 1985 ; Benson, 1984). Diatoms dominated the phytoplankton. Overall algal crop showed a greater concentration in Mandovi as compared to Zuari. It is difficult to present a specific reason for this. Chaetoceros dominated among diatoms followed by Cyclotella and Skeletonema. These species may play an active role in producing arsenite and methylated arsenic compounds also. There is strong evidence of planktonic production of arsenite. Andreae and Klumpp (1979) demonstrated that several species of diatoms

(Skeletonema sp.) and dinoflagellates are capable of producing arsenite.

The differences between estuarine and oceanic arsenic biogeochemistry may be due to differing nutrient strategies of dominant phytoplankton species. Estuarine phytoplankton communities are generally dominated by rapidly growing, opportunistic species with low nutrient affinity especially in summer, when insolation is at a maximum. This growth strategy is successful in estuarine region where low physical stability and relatively high nutrient concentrations prevail. Oceanic communities on the other hand are dominated by species with high affinity for nutrients, adapted for the more stable, low nutrient concentrations found in open Ocean (Fisher, 1977; Guillard & Kilham, 1977; Kilham & Kilham, 1980). Species that exhibit a high affinity for nutrients appear to be better able to discriminate between the necessary and competing ions than do species exhibiting lower nutrient affinity. In the case of arsenate and phosphate, varying degrees of discrimination have been documented for both natural phytoplankton communities (Morris et al, 1984) and for

individual species (Budd and Craig, 1981). Increased ability to discriminate should effectively exclude arsenate from uptake (Morris et al, 1984). Variation in nutrient affinity, therefore suggests that estuarine communities will take up greater quantities of arsenic, which they must then process by reduction, methylation and release. Thus it is logical that estuarine systems will exhibit greater quantities of reduced and methylated arsenic compounds than coastal or oceanic ecosystem.

During the post monsoon, arsenite was found to be in very low concentration in both the estuaries. It varied from 0.04 to 0.15 $\mu\text{g}/\text{l}$ for the surface, while it varied from 0.05 to 0.18 $\mu\text{g}/\text{l}$ for the bottom waters of the Mandovi, the bottom values being high at most of the stations. In Zuari it ranged from 0.02 to 0.06 $\mu\text{g}/\text{l}$ and from 0.03 to 0.09 $\mu\text{g}/\text{l}$ for the surface and bottom waters respectively. Arsenite exhibited a mid estuarine peak in both the estuaries eventhough there is a substantial precipitation. The river runoff is higher compared to premonsoon. The arsenite values are not as high as during the premonsoon. This may be due to the near-

absence of arsenite in rain water, as stated earlier, as well as to the dilution by the river runoff in the premonsoon where the bottom values are higher than the surface values at almost all the stations in Zuari and Mandovi. The values at the riverine end and the marine end are low compared to the values at the intermediate stations. High concentrations of arsenite were consistently observed at M-3 during the study period, both at the surface and bottom waters. Similar high levels were also observed at Z-3. This could be due to the inputs from the mud flats. Station Z-3 is situated at the mouth of the Cumberjua canal. During low tide the banks of the canal at its mouth gets exposed. Because of currents, surface of the mud flat is disturbed. The mid-estuarine maximum observed could be attributed to inputs from these mud flats. The high concentration of arsenite at M-3, Z-3 may also be due to high production as well.

High concentration of arsenite were observed at M-5, Z-4 and Z-5. M-5 is situated near an iron ore loading point where ores are loaded into barges to be transported. High concentration of arsenite at this

station is due to spillage of ore during loading and leaching from the banks.

The postmonsoon months showed the highest number of species of diatoms and dianoflagellates as well as cell counts (Devassy, 1983), which in turn can be related to the high concentration of arsenite in these estuaries. Thus the presence of significant amounts of arsenite is governed by the amount of arsenate present in the estuarine system.

Premonsoon season registered the highest concentration of arsenite while monsoon had the lowest. Concentrations during postmonsoon almost coincided with the values during the premonsoon. It could be seen that during monsoon when the highest water discharge occurred, low concentrations of arsenite were observed; whereas during low discharge i.e. the premonsoon period high concentrations of arsenite were observed.

V.3 DISSOLVED SPECIES-SALINITY RELATION IN THE ESTUARINE SYSTEM

An hypothetical estuary is one which has only two particle -free end- members for mixing at the freshwater ends. In such an estuary the concentration of a particular dissolved substance is a linear combination of the concentration in river and seawater. The real situation in an estuary is complicated by the presence of additional water sources, by gradient in the concentration and suspended matter further by temporal variation in the composition of the mixing, biological activity and varying physical oceanographic conditions (Bewers & Yeats, 1981). Thus deviation from linearity are the result of processes which add or remove the substance from solutions (Evans & Cutshall, 1973). Interactive chemical processes involving the removal or addition of a dissolved constituent in estuarine water have been inferred from non-linear regressions of the dissolved constituent when plotted against a conservative index of mixing such as salinity.

From the data obtained during premonsoon arsenate increased with increasing salinity. It follows the

primary production pattern. Oxygen and carbondioxide are the two important gases in the aquatic environment. The high oxygen value gives an indication of higher photosynthetic efficiency and production, the productivity being higher during premonsoon and postmonsoon and low during the monsoon for both the estuaries (Devassy, 1983). Arsenate and salinity showed a moderately positive correlation ($r = 0.56$) in Mandovi. The linear relationship of arsenate with salinity signify that as salinity increases the arsenate concentration also increases. In oxygenated waters arsenite is oxidised to arsenate which results in high concentrations of arsenate at the marine end. Photosynthetic activity releases oxygen which is an important factor in arsenite oxidation. Heterogenous abiotic reactions may also contribute to the oxidation of arsenite in the estuarine system. Oscarson et al (1981) and Peterson and Carpenter (1983) have shown that the presence of Mn(IV) oxides significantly enhances arsenite oxidation, which may be one of the reason for the high concentration of arsenate at the marine end of the Mandovi. In the Zuari, arsenate profile during the premonsoon was largely conservative and display a near-

linear profile with salinity. Arsenate concentration are nearly constant throughout the estuary, reflecting mixing between end members (0.04 $\mu\text{g}/\text{l}$ arsenate at 6×10^{-3} salinity 0.22 $\mu\text{g}/\text{l}$ arsenate at 35×10^{-3} salinity).

During monsoon the behaviour was different. During the monsoon, an addition to the estuary was noticed alongwith the removal at the lower salinities. The main contribution is from the stations upstream. The concentration of arsenic in the iron ore sample analysed was 50 $\mu\text{g}/\text{g}$ and hence the partial dissolution of the mining rejects could lead to high concentration of arsenic at the riverine stations. During monsoon because of the precipitation, high river runoff and strong winds there could be drastic changes in the estuarine conditions within a very short time. This could be the reason for the different behaviour of arsenate.

During the premonsoon and postmonsoon the estuaries are fed by seawater. There is a strong increase of arsenic concentration towards lower salinities of the estuaries. The negative concentration resulted from the

removal of AS⁺⁵ from solution at low salinities. Arsenic may also be co-precipitated with Fe. This phenomenon has been described as an important mechanism for arsenic removal from solution (Crececius et al 1975). The waters of Mandovi and Zuari are very rich in dissolved iron and manganese because of the mining activities (Anon, 1979). When river water of typical pH 6-7 mixes with the seawater having a pH of 8, hydrolysis of Fe (III) is one of the most likely reaction taking place. Precipitation of iron have been reported by many workers (Windom et al. 1971, Holiday and Liss, 1976). These hydrogenous oxides are very effective in the removal of trace elements from solution in natural waters (ANON, 1975). Co-precipitation with iron hydroxide could have lead to a low concentration of arsenate at the high salinity region of the Mandovi and Zuari.

Arsenate, the stable form in aerobic water, may be removed by several mechanisms. La Peintre (1954) showed that arsenate species coprecipitate with or adsorb onto hydrous iron oxides. Shnyukov (1963) observed that iron ores are always enriched in arsenic owing to the high

adsorptive capacity of the hydrous iron oxide, while arsenic is nearly absent from manganese ores. The fact that iron oxide has a positive surface charge in most geologic environments and preferentially adsorbs anions, while manganese oxide is negatively charged and adsorbs cations, has been cited as an explanation of such distribution of arsenic (Goldschmidt, 1937).

The correlation between arsenate and salinity was + 0.56, - 0.64 and - 0.76 for the premonsoon, monsoon and postmonsoon respectively. The negative correlation coefficients reveal that arsenic was removed in both freshwater and estuarine waters and that river is the source of the metalloid. Arsenic removal or addition with salinity is shown in Fig. 14-16. Arsenate removal is observed in 81% of samples collected during the monsoon and 90% of samples collected during the postmonsoon, which is quite similar to the observations of Fondekar and Reddy (1974) in Zuari estuary. From these observations it appears that the inverse in species predominance take place at low chlorinities. Sharp changes in the ionic strength during early mixing seem to be important in this respect. Removal of arsenate

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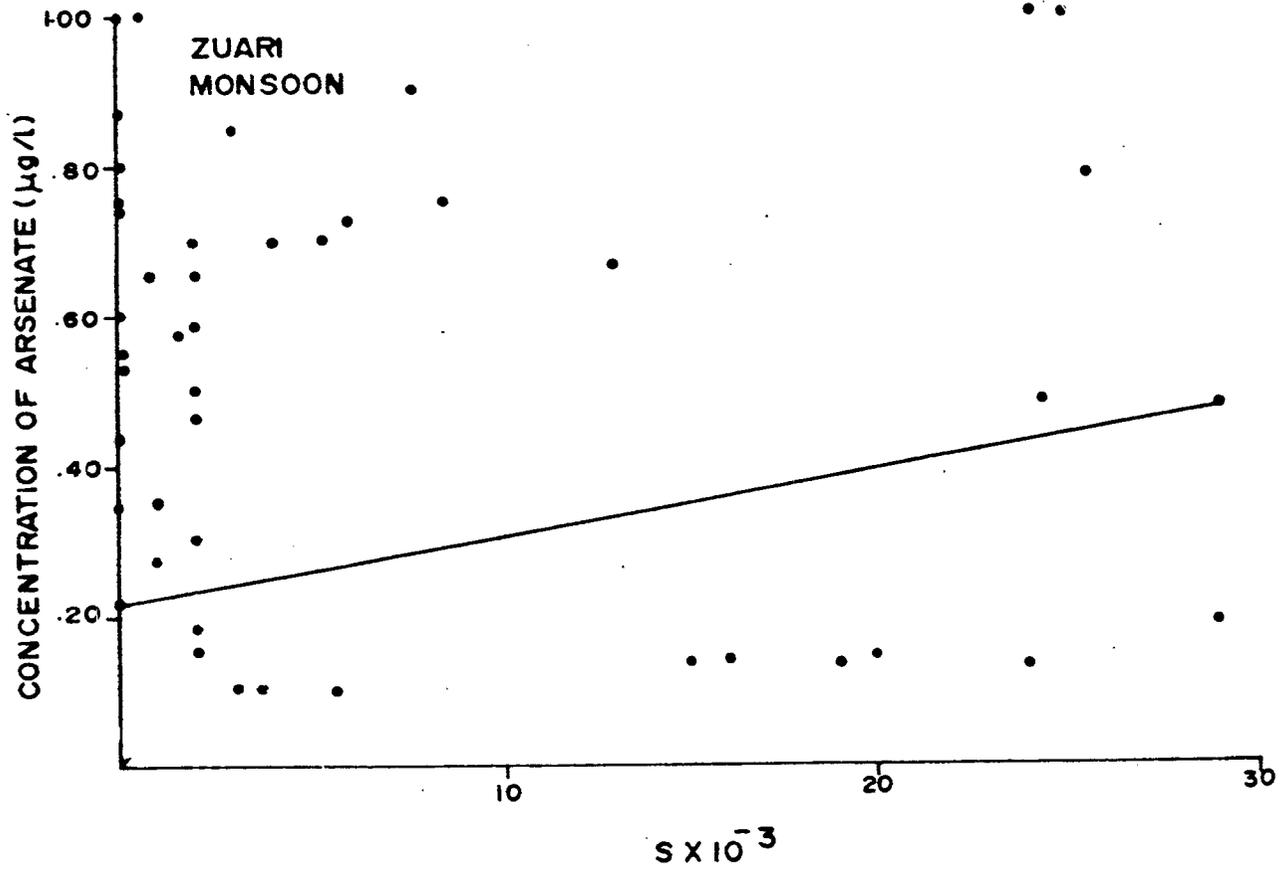


Fig.15

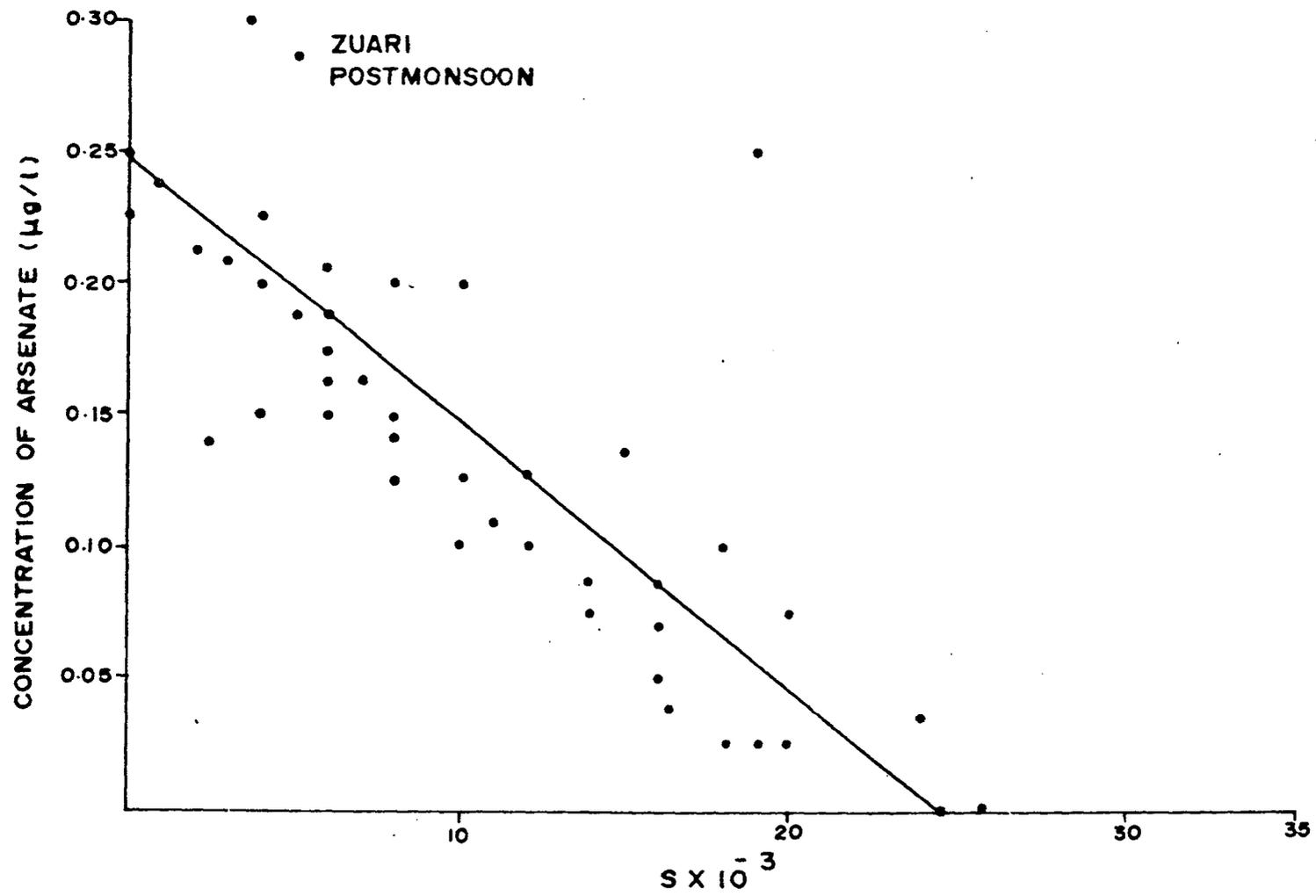


Fig.16

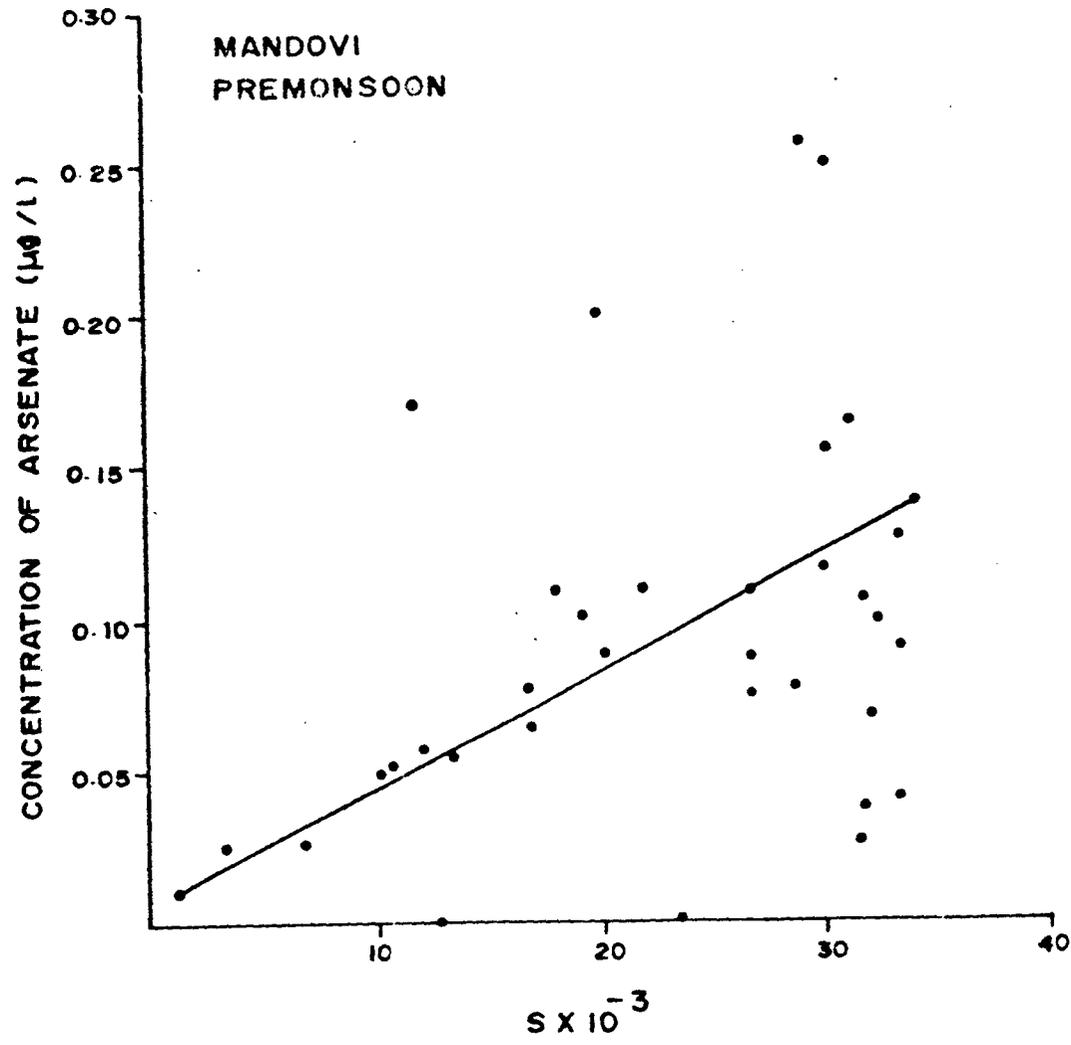
have also been reported by other workers. In the iron-rich estuary of the river Beaulie (Hampshire, U.K.) (Howard et al. 1984) extensive removal of arsenic has been demonstrated together with strong seasonal variations in the appearance of arsenic (III) and methylated species (Howard et al., 1982).

In four estuaries in the south-eastern U.S.A. (Waslenchuk and Windom, 1978), however, arsenic was shown to behave conservatively, a fact that was ascribed to the blocking of arsenic binding sites by low molecular weight organic matter.

During the postmonsoon season there was a net removal in the salinity range $15 - 25 \times 10^{-3}$. During most of the time the main source was at the upstream stations. Tailings from the mines located upstream could lead to a high concentration of arsenate at the riverine stations.

In Zuari too, there was a mid estuarine maxima during the premonsoon. The plot show appreciable scatter with high arsenate values in the salinity range $14 - 20 \times 10^{-3}$. Points corresponding to samples in the

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salinity range $13 - 20 \times 10^3$ show a tendency to fall below the theoretical dilution line indicating possible removal from the system.

Arsenite for the different seasons did not reveal any particular trend in both the estuaries as seen in Fig. 17-23. Being reduced species it is not thermodynamically stable. Concentration of arsenite in both these estuaries are very low. These are mainly dominated by arsenate, which is the most stable form of arsenic in the water column. During the monsoon there was a removal at the lower salinities of both the estuaries. During most of the time the main source was the upstream stations.

During the postmonsoon there was a clear sign of addition of arsenite. At the high saline region, however, addition decreases. This was evident in the Zuari. However no meaningful inference could be obtained from the plot of the Mandovi estuary.

V.4 ARSENIC IN OCEANIC AND COASTAL WATERS

The composition of the world oceans is largely controlled by the input of material carried by rivers.

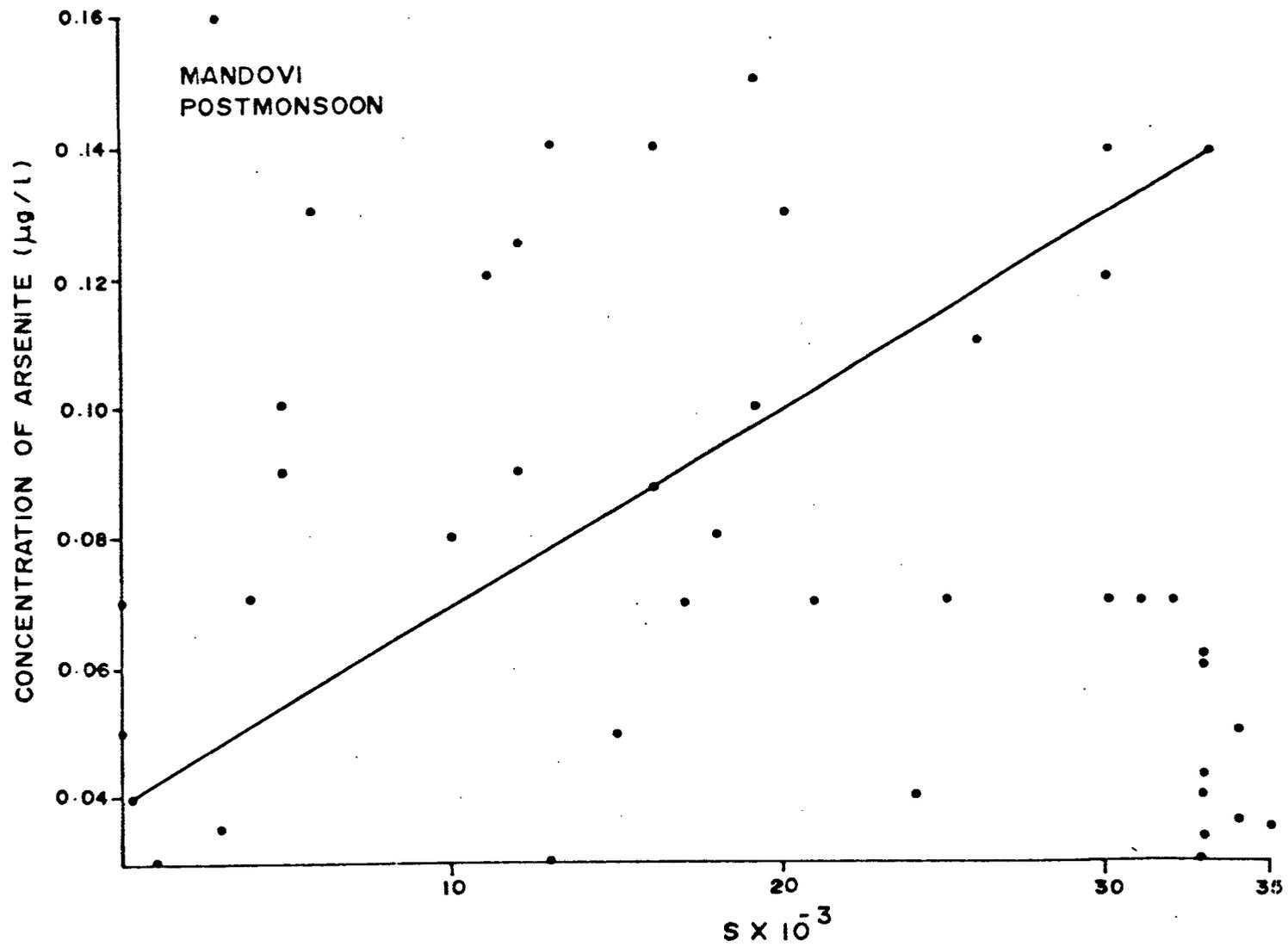
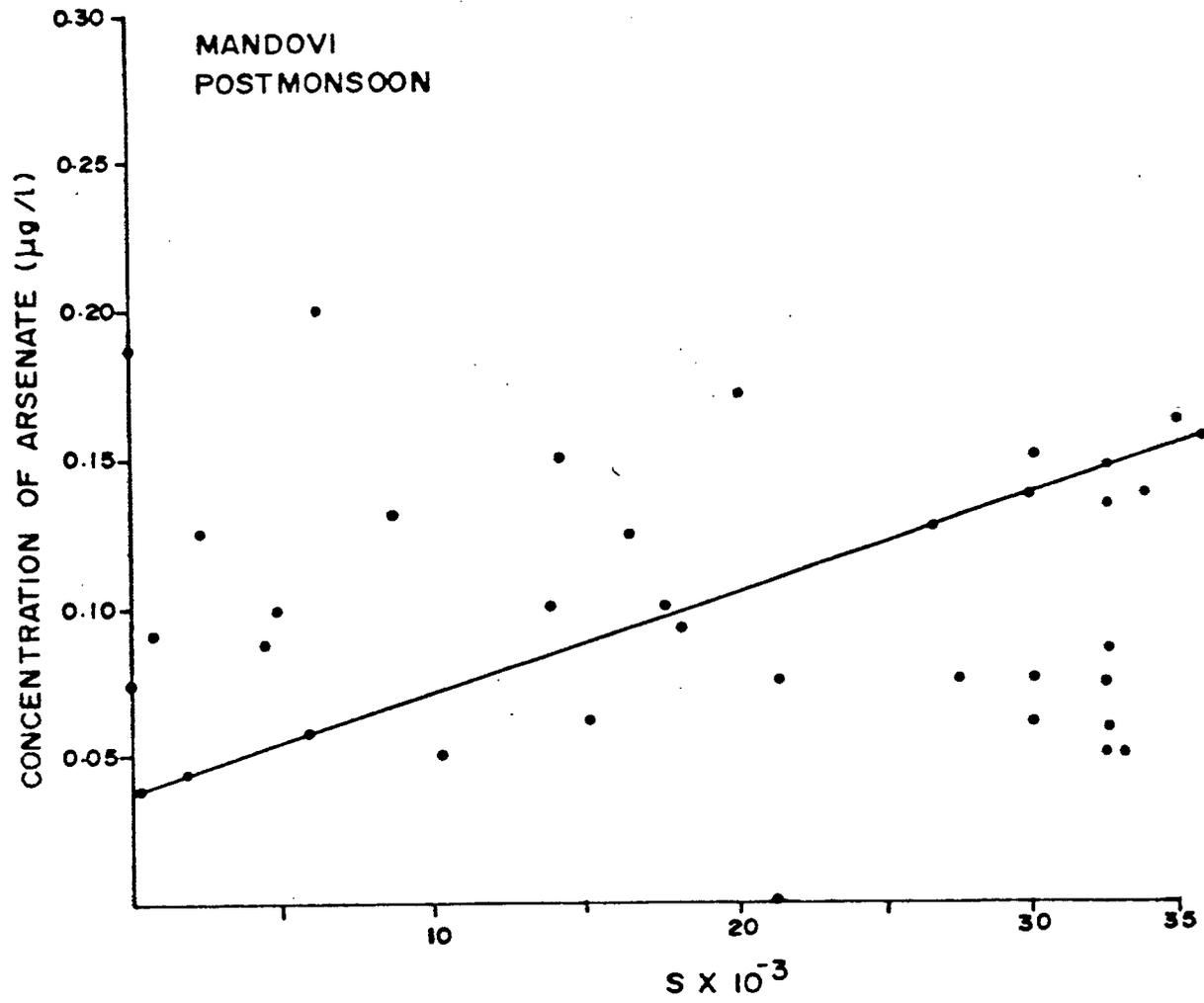
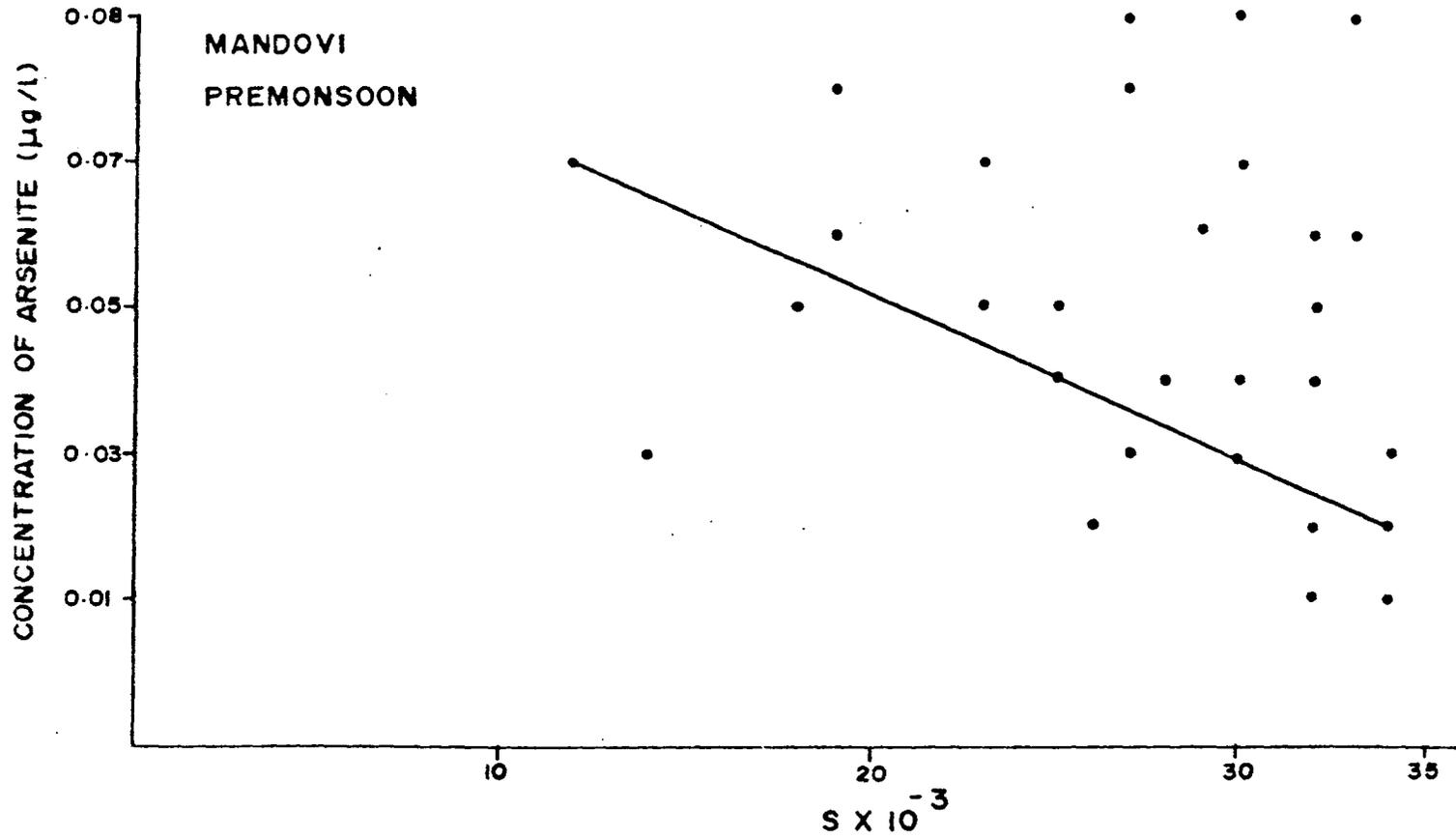


Fig. 17





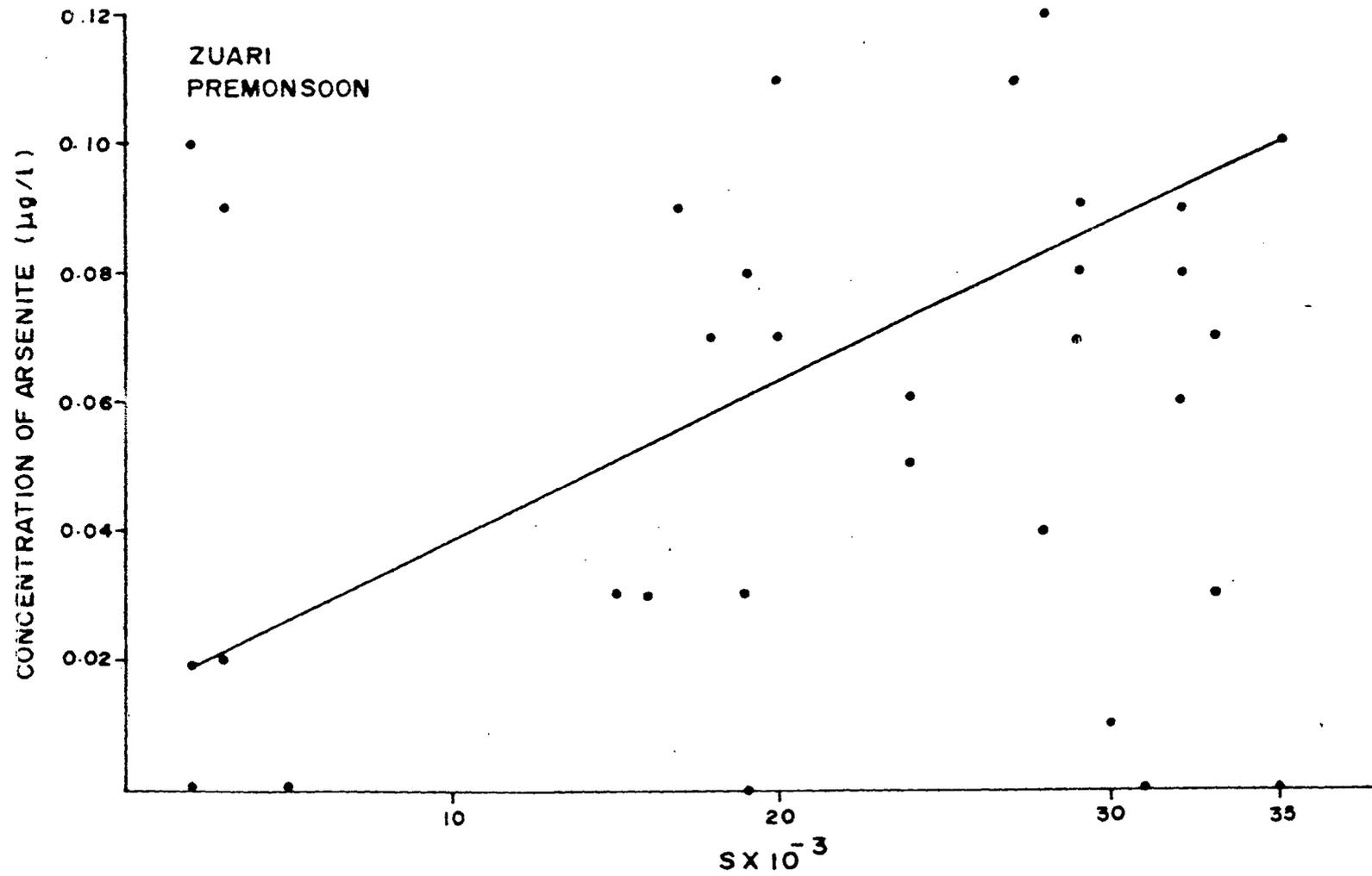


Fig. 20

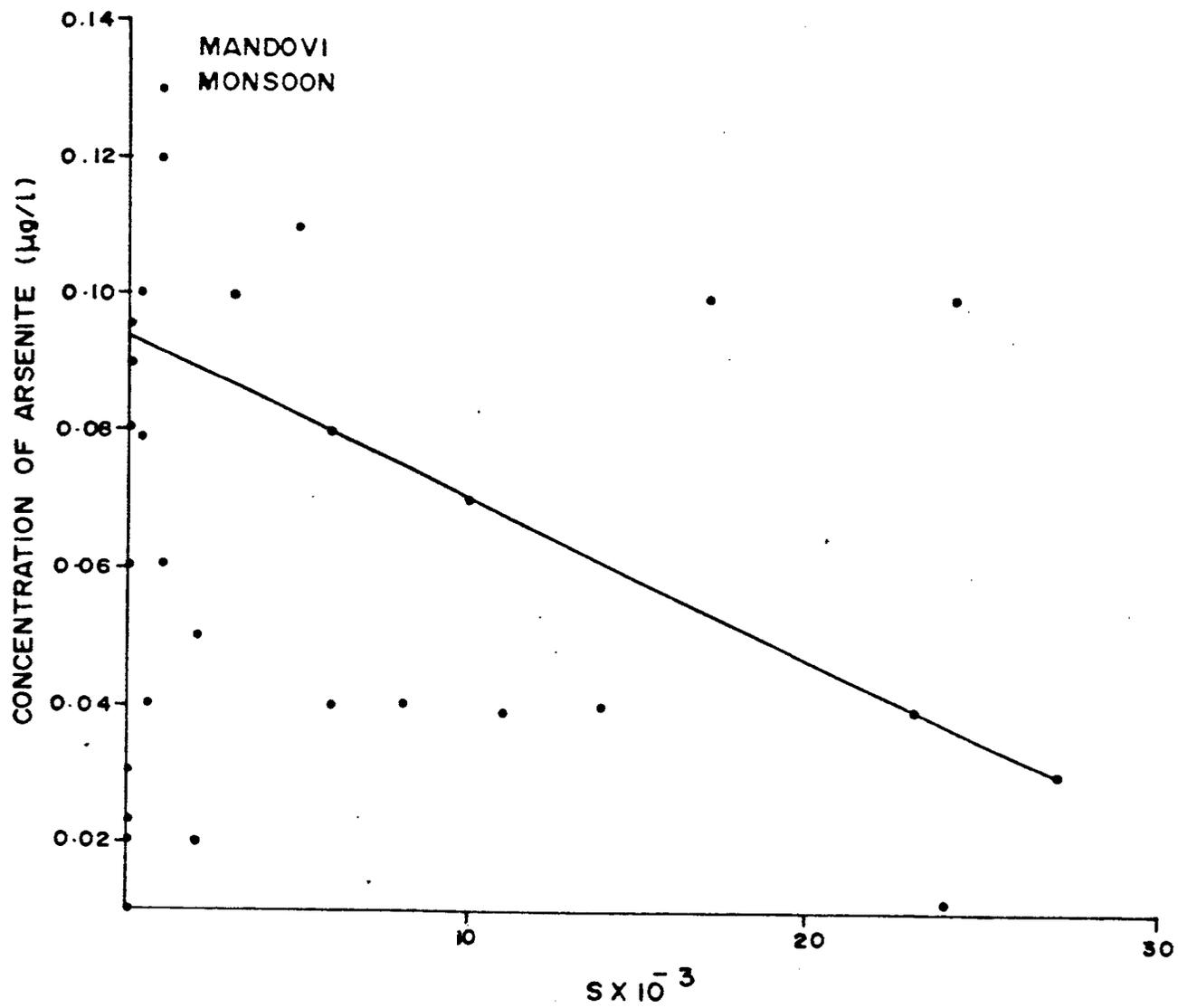


Fig. 21

ZUARI
MONSOON

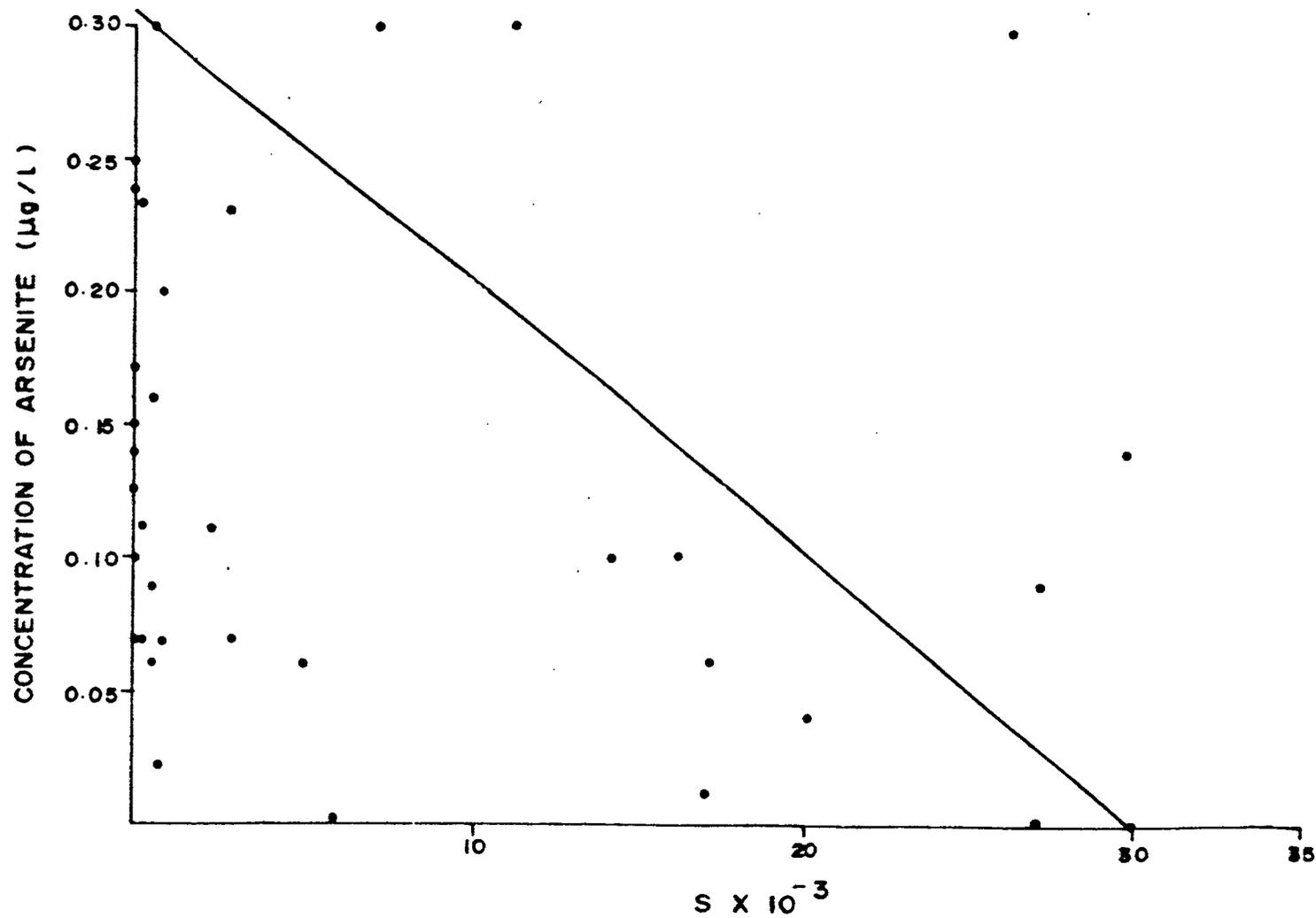
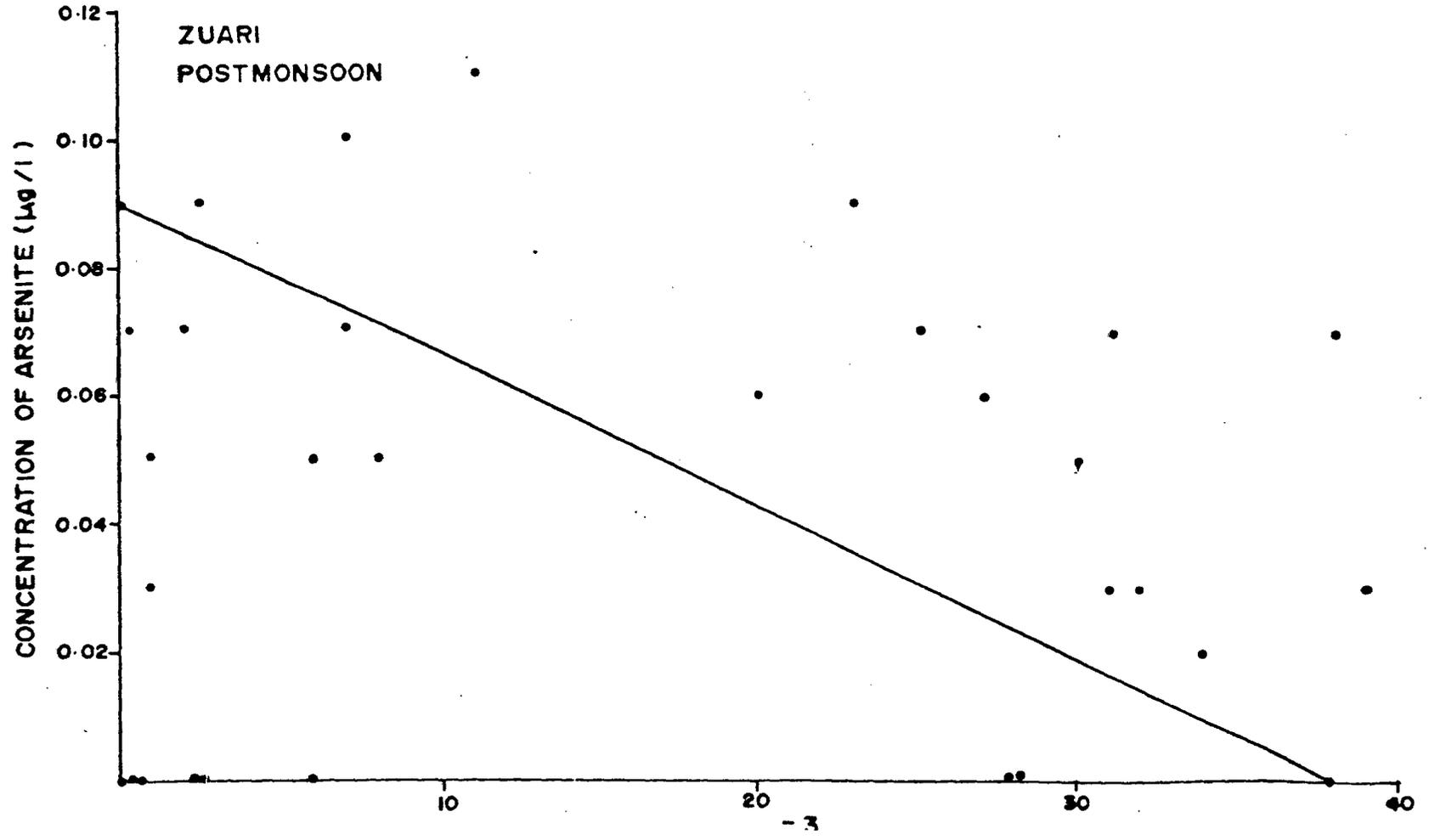


Fig. 22



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Man alters the river inputs into the oceans by adding pollutants to the water discharged from the continents. Estuaries and coastal areas can act as barriers for metals carried by rivers removing materials into the sediments before they enter the oceans. Coastal areas provide a variety of environments with fundamentally different conditions, capable either to 'trap' in a restricted area considerable amount of metals or to affect their speciation drastically (Scoullou, 1983). In this respect studies on trace metal concentrations in coastal areas are assuming greater significance. Moreover, the data collected could form a baseline for the coastal waters of India.

The area studied is covered by a few stations along the West Coast of India as shown in Fig.24 , and coastal areas off the mouth of Mandovi and Zuari.

RESULTS

The data for arsenate and arsenite are listed in Tables (9 & 10). Variations in concentration of arsenate and arsenite with locations and depth are small

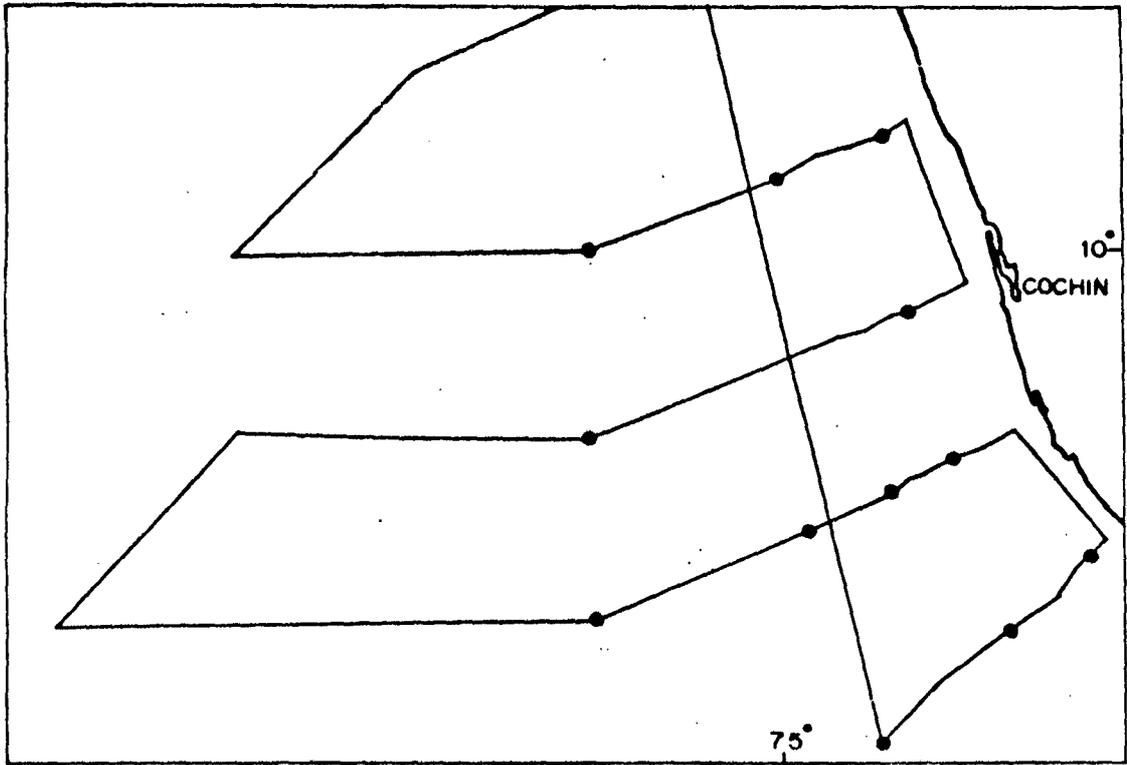


Fig.24 STATION LOCATIONS ALONG THE WEST COAST

TABLE - 9

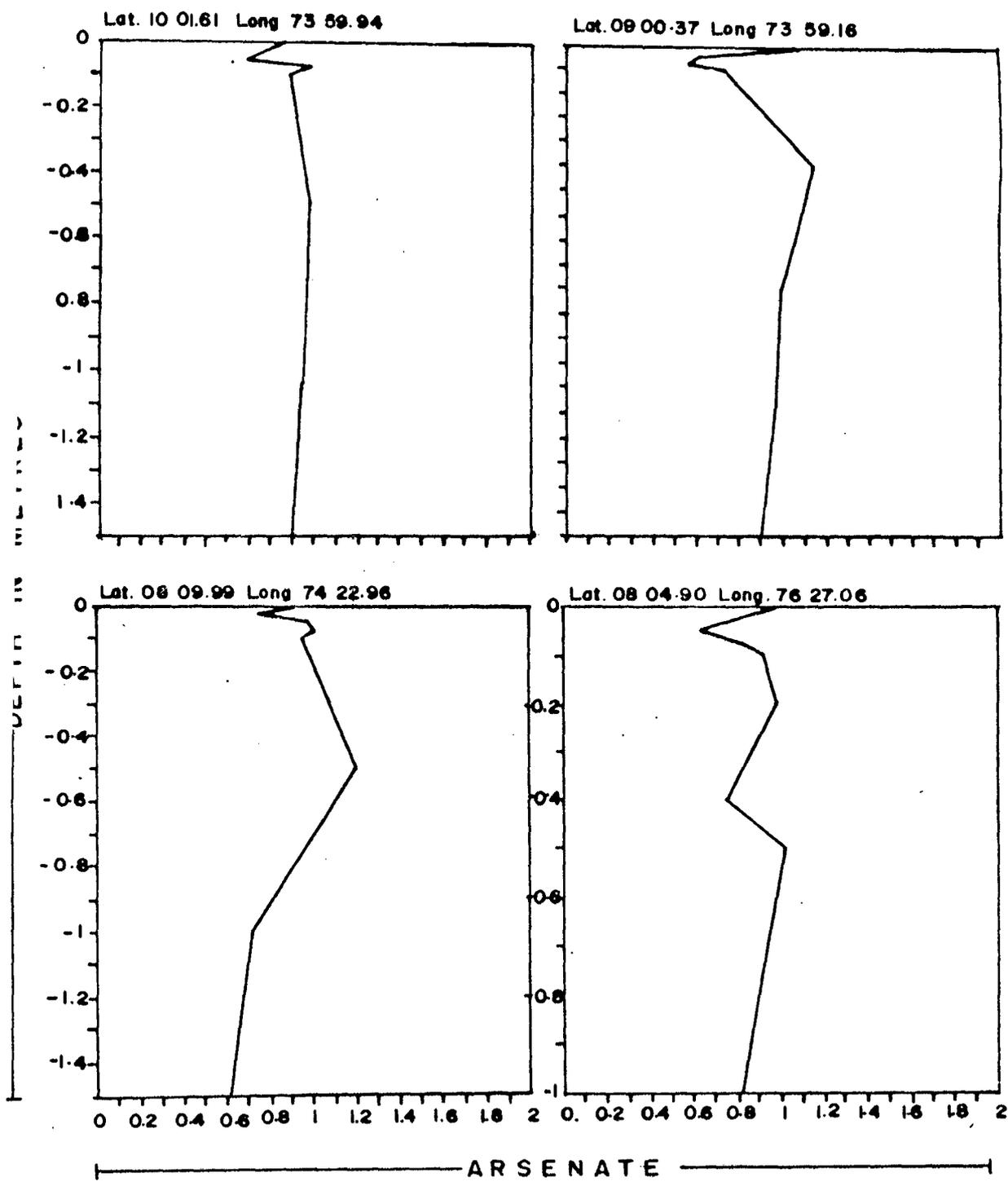
Arsenic concentrations in Oceanic waters ($\mu\text{g/l}$)

St. No.	Depth	Arsenate	Arsenite
6	0	1.00	0.03
	50	0.63	0.04
	75	0.82	0.04
	100	0.92	0.09
	200	0.98	0.02
	400	0.75	N.D.
	500	1.02	0.09
	1000	0.82	N.D.
10	0	1.03	0.06
	25	0.92	0.03
	50	0.94	0.04
13	0	0.95	0.07
	25	1.02	0.06
	50	1.03	0.05
16	0	1.00	0.04
	25	0.70	0.07
	50	0.63	0.02
	75	0.97	N.D.
	100	0.87	N.D.
	200	1.07	N.D.

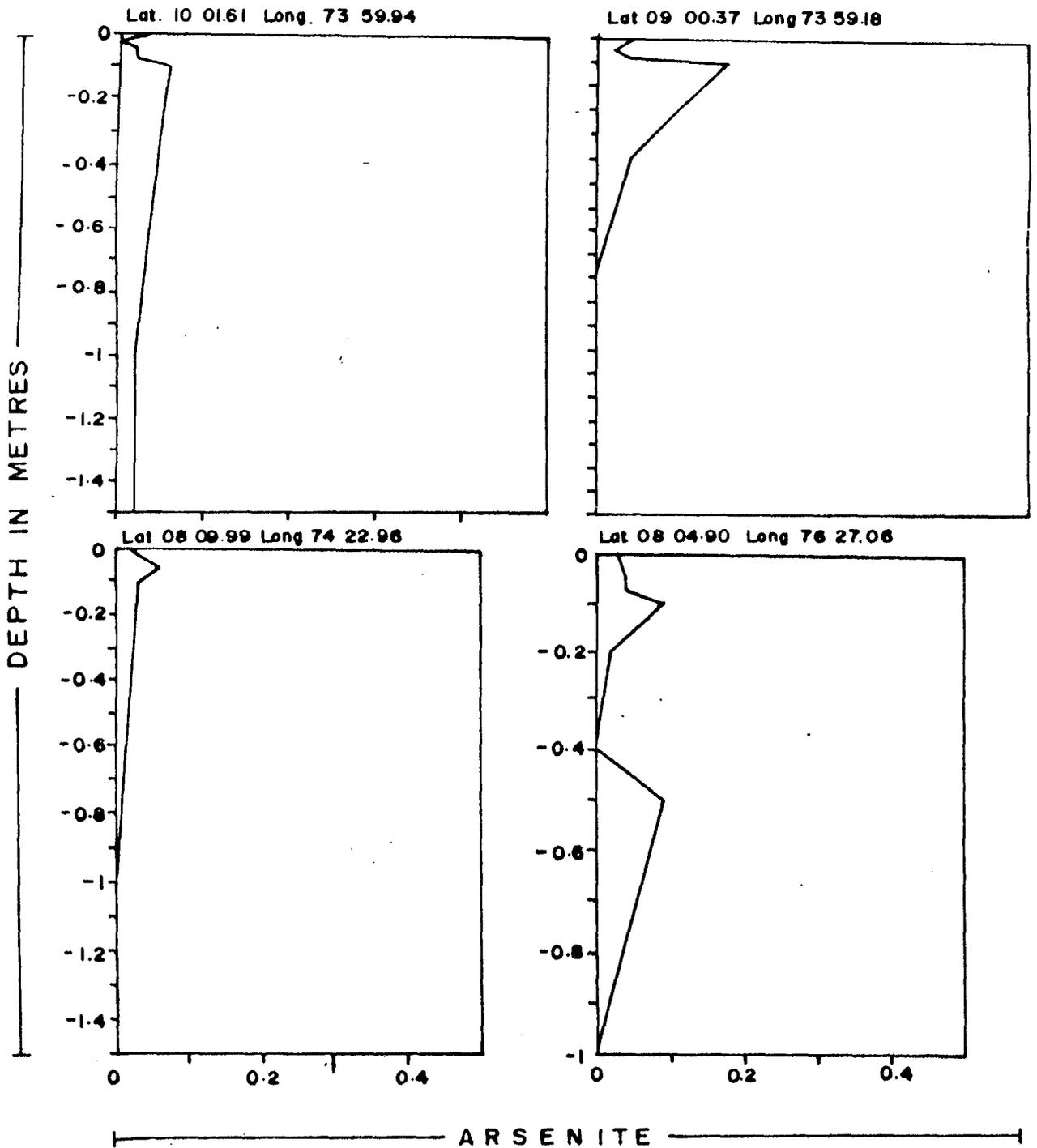
St. No.	Depth	Arsenate	Arsenite
22	0	0.98	0.02
	25	0.75	0.03
	50	0.97	0.06
	75	1.00	0.05
	100	0.95	0.03
	500	1.20	0.02
	1000	0.72	N.D.
	1500	0.62	N.D.
29	0	1.13	0.05
	25	0.98	0.03
	50	0.62	0.02
	75	0.57	0.04
	100	0.73	0.15
	500	1.15	0.04
	1000	1.00	N.D.
	1500	0.97	N.D.
34	0	0.87	0.07
	25	0.93	0.06
	50	0.57	N.D.
	75	0.50	N.D.
	100	0.95	0.02

St. No.	Depth	Arsenate	Arsenite
	200	0.96	N.D.
38	0	0.57	0.07
	10	0.57	0.05
	25	0.63	0.02
48	0	0.85	0.04
	25	0.79	N.D.
	50	0.68	0.02
	75	0.99	0.02
	100	0.89	0.06
	1000	0.98	0.04
	1500	0.96	0.02

N.D. - Non detectable



VERTICAL PROFILES OF ARSENATE



VERTICAL PROFILES OF ARSENITE

and there is no indication of clearly defined maxima in the water column. In the oxic zone arsenate is the most abundant oxidation state of the element. However, reduced forms of arsenic (arsenite) is present at detectable levels throughout the water column. At most of the stations arsenite concentrations show little variation with depth. An increase of arsenate with depth is evident down to about 1000m. Except for a small amount of arsenite all the dissolved arsenic is in the arsenate form. The depletion of arsenate may be due to the rates of arsenate uptake and release by the biota. Arsenate in the deep ocean show little variation. And increase of arsenate with depth is evident down to about 1000m, while the surface values were high for most of the stations ranging from 0.85 to 1.13 $\mu\text{g}/\text{l}$. Small decrease in arsenate and increase in arsenite are found in the waters at 75m depth. Surface depletion of As (V) has also been reported for the south Atlantic (Statham, et al, 1987), the Indian Ocean (Hoede, et al, 1987) and the Pacific Ocean (Anderea, 1979). This depletion is often attributed to biological activity since the uptake of arsenic by biota in the euphotic zone is small, compared to the amount of

arsenic present there. The degree of depletion is not significant in near-shore stations, higher concentrations were frequently observed. Arsenate either increased offshore or remained more or less constant at each station. The average reported value for seawater (Indian Ocean) is 3 $\mu\text{g}/\text{l}$ (Onishi, 1955). The values observed (av. 2.5 $\mu\text{g}/\text{l}$) during this study are quite comparable to those reported from other areas.

In the Arabian Sea the dissolved oxygen concentration at an intermediate depth (about 150 - 1000m) is extremely low, often below the detection limit of the conventional analytical method. In this layer many of the components of seawater undergo changes and are often present in their reduced forms. Presence of As^{+3} along with As^{+5} can be the effect of this oxygen minimum water mass as well.

Coastal waters of Goa

The variations in the concentrations of arsenate and arsenite were much lower in this area compared to other regions studied. Arsenic concentrations in the

coastal waters showed wide variations. Arsenate concentrations off Aguada varied from 0.06 to 0.22 $\mu\text{g}/\text{l}$ for the surface, while for the bottom it varied from 0.06 to 0.33 $\mu\text{g}/\text{l}$. Off Marmugao arsenate was low in concentration varying between 0.01 to 0.25 $\mu\text{g}/\text{l}$ and from 0.05 to 0.22 $\mu\text{g}/\text{l}$ respectively. Arsenite was however on the lower levels or below the detection limit at most of the stations. Maximum concentrations observed at the surface was 0.13 and for the bottom it was 0.14 $\mu\text{g}/\text{l}$ off Marmugao. Off Aguada the arsenite concentration varied from below detection limit to 0.04 and from 0.00 to 0.08 $\mu\text{g}/\text{l}$ at a surface and bottom waters respectively. The kinetics of the arsenite -arsenate transformations in the oceans are not well understood. Both bacteria (Johnson, 1972) and marine phytoplankton (Andreae & Klumpp, 1979) can reduce arsenate to arsenite, and the reverse reactions is known to be catalysed by a number of bacteria (Osborne & Ehrlich, 1976). Johnson & Pilson (1975) observed the oxidation of arsenite to arsenate in seawater given under sterile conditions; but the oxidation rates decreased drastically after a few days. This effect was most pronounced at the lowest concentrations they used (0.86 μm) which was still four

TABLE - 10

Arsenic in the coastal waters of Goa ($\mu\text{g/l}$)

Station	Months	Arsenate		Arsenite		
		Surface	bottom	surface	bottom	
Off Aguada 1987	February	0.15	N.D.	N.D.	0.08	
	March	0.22	0.23	0.03	0.06	
	April	0.04	0.07	N.D.	N.D.	
	1988	February	N.D.	0.06	N.D.	N.D.
		March	0.12	0.33	N.D.	0.03
		April	0.06	0.22	0.04	0.07
Off Mormugao 1987	February	0.05	0.06	N.D.	N.D.	
	March	0.05	0.06	0.13	0.14	
	April	0.10	0.13	0.10	0.14	
	1988	February	0.01	0.05	0.10	0.07
		March	0.25	0.05	N.D.	N.D.
		April	0.06	0.22	0.08	0.10

N.D. - Non detectable

Correlation Coefficients

	PREMONSOON	MONSOON	POSTMONSOON
<u>Mandovi</u>			
Salinity vs Silicate	-0.99	-0.95	-0.94
Salinity vs Phosphate	0.66	-0.43	-0.43
Salinity vs Arsenite	0.09	-0.38	-0.29
Salinity vs Arsenate	0.56	-0.64	-0.76
<u>Zuari</u>			
Salinity vs Silicate	-0.98	-0.93	-0.98
Salinity vs Phosphate	0.06	-0.60	-0.17
Salinity vs Arsenite	-0.11	0.61	-0.50
Salinity vs Arsenate	-0.25	-0.66	-0.60

~r' values < + 0.70 insignificant.

orders of magnitude higher than arsenite concentrations in seawater.

Arsenate and arsenite concentrations were much lower in the coastal waters of Goa. There was a decrease in the concentrations from the mouth of the river to the coastal stations because of the ongoing dilution. Local geological and climatological variations may affect the trace metal inputs into the coastal waters.

V.5 ARSENIC IN THE ESTUARINE SEDIMENTS

Estuarine sediments are sinks for many materials transported from the land. Trace metals are mobilized as a result of natural processes as well as by anthropogenic inputs and thus become enriched in estuarine and coastal sediments. The contributions of trace metals in natural estuarine and coastal marine sediments are determined by inorganic detrital, rather than organic and non-detrital materials. The inorganic detritus is the result of chemical and physical weathering of continents and is composed of quartz,

feldspars, pyroxenes, micas and clay minerals and small amounts of metal oxide and sulphide phases (Windom et al., 1989).

The concentration of arsenic in soils is typically 0.1 - 4.0 mg/kg (dry wt) but can be greatly elevated in mineralized areas (Woolson, 1983). Levels in freshwater lake sediments might be expected to reflect the naturally occurring arsenic content of the soils of the corresponding catchment areas, except where there is significant input from nearly industrial (eg. smelting, mining) or agricultural (eg. pesticides application) activities.

Analysis of soils from the Mandovi-Zuari catchment areas showed an elevated level of arsenic 9.48 $\mu\text{g/g}$ (dry wt). This soil sample is obtained from the mining areas of Mandovi, while the samples obtained slightly away from the mining areas revealed a concentration of 7.93 and 5.58 $\mu\text{g/g}$ (dry wt) of arsenic. This explains the occurrence of high level of arsenic towards the upstream stations of the Mandovi and Zuari estuarine system.

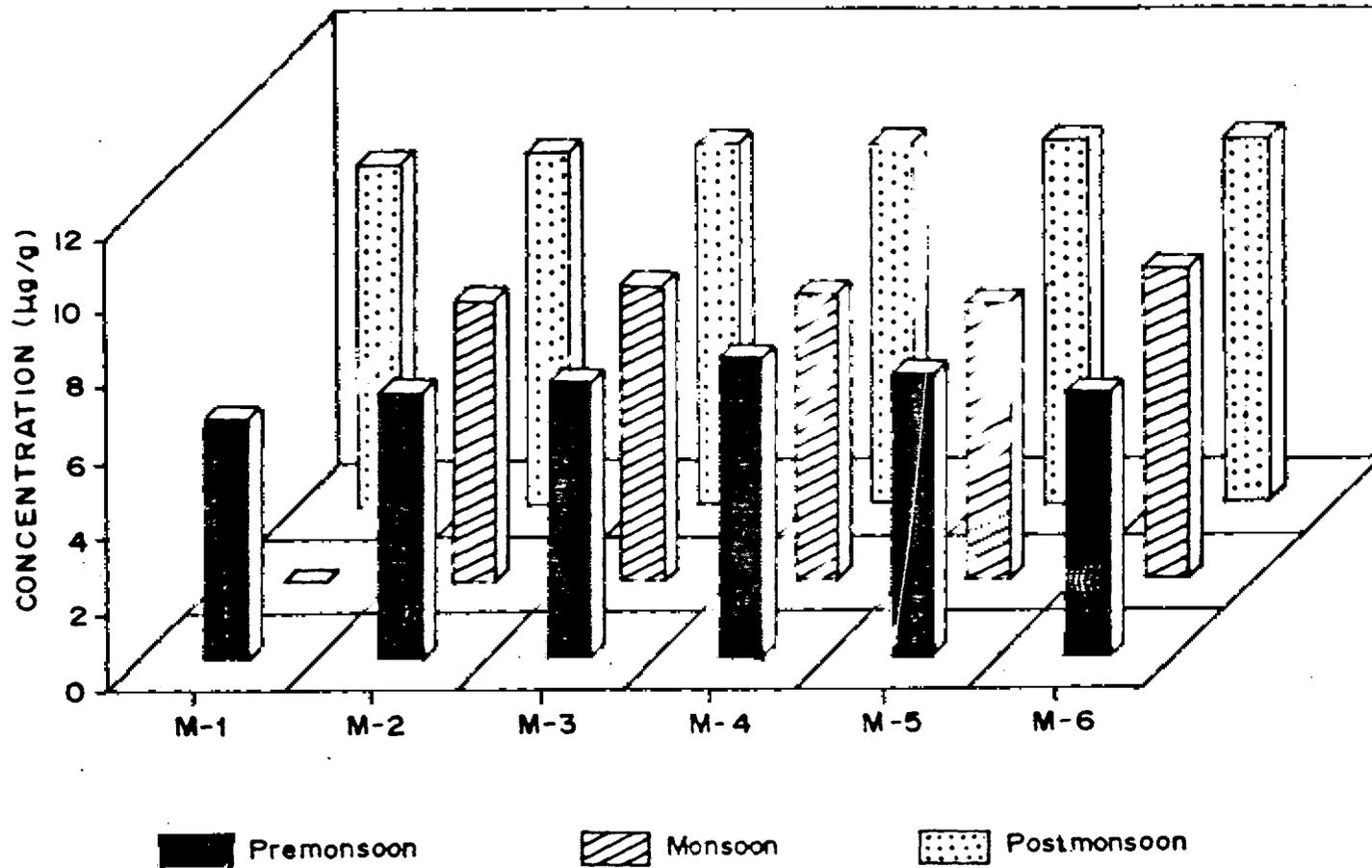


Fig. 25

CONCENTRATION OF ARSENIC IN SEDIMENTS OF MANDOVI.

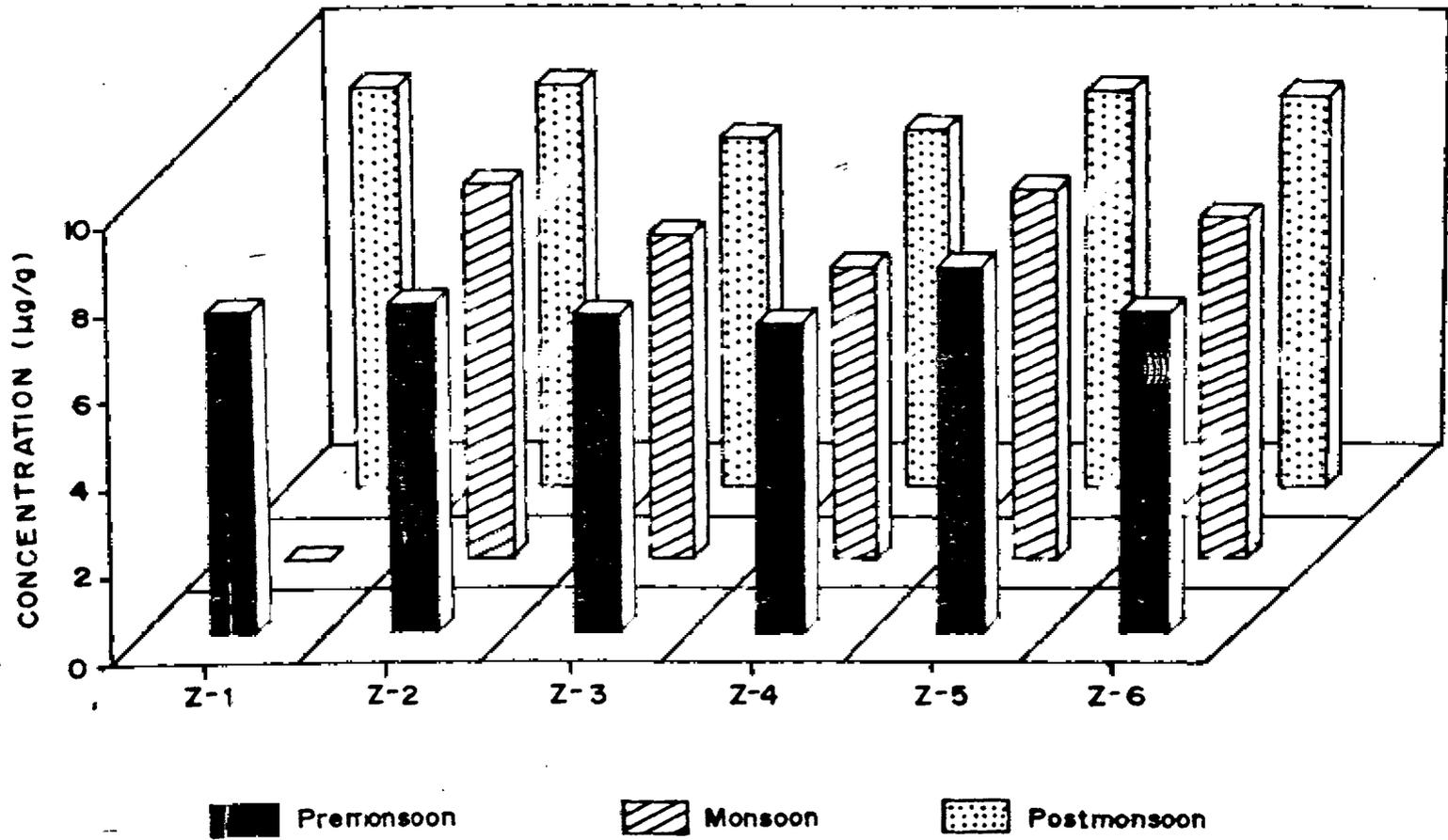


Fig. 26 CONCENTRATION OF ARSENIC IN SEDIMENTS OF ZUARI

Loss of inorganic arsenic from seawater has generally been attributed to adsorption of arsenic on iron oxide surface followed by sorption of the iron-arsenic complex by suspended sediment particles (Angelidis and Grimanis, 1987). Andreae (1979) found that the total arsenic was lower in interstitial waters than in the overlying waters and attributed this to the removal of arsenic into the sediments either by adsorption or coprecipitation. This mechanism was probably operating only in uncontaminated sediments. This observation was made by Crecelius et al., (1975). This holds good for the Mandovi-Zuari sediments also. Arsenic preferentially adsorbs onto Fe oxide as compared to other suspended particulates (Crecelius et al., 1975). This preferential behaviour of arsenic towards Fe oxides can be explained on the basis of charge on the Fe oxide surfaces. Hydrous Fe oxide has a zero charge at pH 8.6 (Kinniburgh et al., 1976) and thus a net positive charge in aquatic systems with pH < 8.6 such as marine sediments and seawater. Arsenic in seawater exists in anionic form (negatively charged) and therefore can be adsorbed onto the surface of hydrous Fe oxides. Jayakumar (1987) in his work observed that Fe

(III) brought by the river cannot exist in free state. It is generally held in stable complex solution, otherwise Fe (II) forms hydrous oxide precipitate. Hence the high concentration at station M-5, M-6 and Z-6 could be due to the hydroxide precipitates from the weathering zone brought by the river and from the nearby mine areas. Hence high values observed at the freshwater region is a positive proof of significant uptake of arsenic by the sediments from the adjoining land.

In oxic surface sediments arsenic is strongly associated with iron presumably in the form of arsenate adsorbed on ferric oxides and hydroxides or of precipitated FeAsO₄ (Kanamori, 1965; Ferguson and Gavis, 1972; Crecelius, 1975; Price, 1976). Hence the high values of arsenic at station M-5 and Z-6 could be from the iron oxide particles coming from the processing plants and loading points at these stations. As stated earlier arsenic concentration in the iron ore is not very insignificant (50 µg/g). In Zuari the high concentration of arsenic is in the saline end and

freshwater end with low values at the intermediate stations.

During the monsoon the arsenic in the sediments of both the Mandovi and Zuari show the same trend with high values at the marine end, with a maximum at station M-5 and Z-4 and increasing towards the freshwater end. The values ranged from 7.30 to 8.24 $\mu\text{g/g}$ (dry wt) in the Mandovi, while that in Zuari ranged from 6.68 to 8.56 $\mu\text{g/g}$ (dry wt).

During the postmonsoon the concentration is higher throughout the estuary. This trend is the same for Zuari also. The values ranged from 9.27 to 9.72 $\mu\text{g/g}$ (dry wt) for the sediments of the Mandovi; while that of the Zuari is from 7.97 to 9.22 $\mu\text{g/g}$ (dry wt).

Low values observed during the monsoon is due to the dilution by rain water. Aston and Chester (1973) found that in the absence of sediment particles the rate of removal of dissolved iron decreased. The implication of this result on the natural processes, is that, iron removal is more likely to be heterogenous nucleation on natural suspended sediment particles than by formation

of a floc of iron hydroxide. These particles settle down when they reach saline waters. This could be the reason for the high values observed at the mouth of the estuaries.

Arsenic has been measured in estuarine sediments ranging over three orders of magnitude with the highest value occurring in areas of mining activities. Aston et al., (1975) found similar distribution of arsenic in a semi quantitative study of freshwater streams, where the occurrence in sediments reflected the contribution of overlying waters. The most probable source of arsenic in these estuarine waters was considered to be from dissolution of arsenic ores.

The transport of arsenic into estuaries by suspended matter has been established (Creceius et al., 1975; Waslenchuk, 1979). Flocculations of suspended matter and colloidal material containing Fe-sesquioxides and organic material occurs on mixing of river and seawater (Picard and Felbeck, 1975; Sholkovitz, 1978). Heterogenous precipitates of ferric hydroxide have also been found on sediment particles in the Beaulieu estuary (Holiday and Liss, 1976) which may act as collectors for

arsenic in and out of the water column before the material is deposited. This could represent a direct input of arsenic to the estuarine sediments.

The fixation of arsenic in marine muds 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 freshwater 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.

Generally the amount of trace metals in sediments is controlled by the elemental solubility in the waters, feeding capacity of the drainage basins and the prevailing environmental conditions. In clay minerals the trace elements are concentrated by adsorption-chemisorption and iron-exchange processes. The

precipitating manganese and ferric oxides may entrap arsenic. Plankton readily extract trace metals from sea water. These organisms on decay settle to the bottom and the trace metal is released and added to the sediment by chelation and other processes. This could be one of the reasons for the high values at the marine end of the Zuari estuary namely Z-1 and Z-2, during the postmonsoon period. Burton and Liss (1976) stated that arsenic form stable bonds with organic sulphur and therefore remain in sediment with high organic content.

The source of organic carbon to the surface sediments can be land runoff, precipitation from water and biogenic changes within the sediment. The average values of organic carbon is given in Table 11. The high organic content at the mouth region can be ascribed to the high productivity of the overlying waters, weak tidal currents, high oxygen and sediments of sand-silt to sand-silt-clay nature. Hence the high values of arsenic observed at the mouth region of the estuary is attributed to this. The organic carbon content of the sediment of Mandovi varies from 1.37 to 2.66% (dry wt) during the premonsoon varying from 0.65 to 1.76. The

TABLE - 11

Average values of organic carbon (%) off Mandovi & Zuari

	PREMONSOON	MONSOON	POSTMONSOON
<u>Mandovi</u>			
1) M-1	2.66	0.65	1.27
2) M-2	1.64	1.37	2.19
3) M-3	1.51	1.02	0.94
4) M-4	1.82	0.74	1.36
5) M-5	1.56	1.76	1.94
6) M-6	1.37	0.85	2.46
<u>Zuari</u>			
1) Z-1	1.70	0.55	1.27
2) Z-2	1.42	1.22	1.69
3) Z-3	1.35	0.85	1.01
4) Z-4	1.55	0.70	1.32
5) Z-5	1.28	1.45	1.76
6) Z-6	1.26	0.81	2.02

postmonsoon values varied from 1.27 to 2.46% in the Zuari. During the postmonsoon the upstream stations had a high organic carbon content, which may be due to the effect of land runoff. The values of organic carbon content in the sediment of Zuari are comparatively less. This is because the influence of sea water is more in Zuari and hence production is less. Therefore, it is clear that organic carbon plays a role in the distribution of arsenic in the sediments of the estuaries.

The plot of arsenate vs total arsenic in sediments (Fig.27,28) during the monsoon showed a clear linear relationship in both the estuaries. It indicates the dominance of As^{+5} in the total sediment arsenic pool. Effective leaching of arsenate is taking place; which appears to be more prominent in Zuari (intercept on the Y axis). The arsenic brought in by the rivers is getting leached at the lower salinities of the estuaries. As salinity increases dissolution comes down. Desorption is due to the flow of freshwater during the period of maximum precipitation. Thus the sea water does not have any effect on the concentration

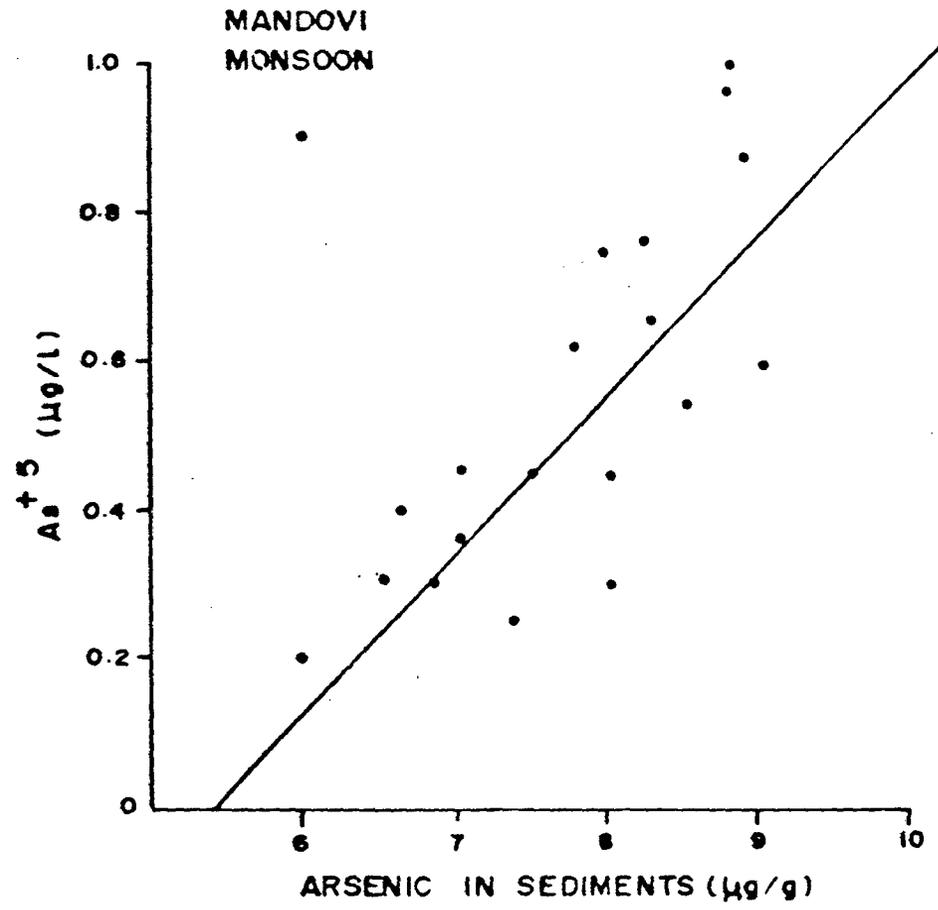


Fig.27

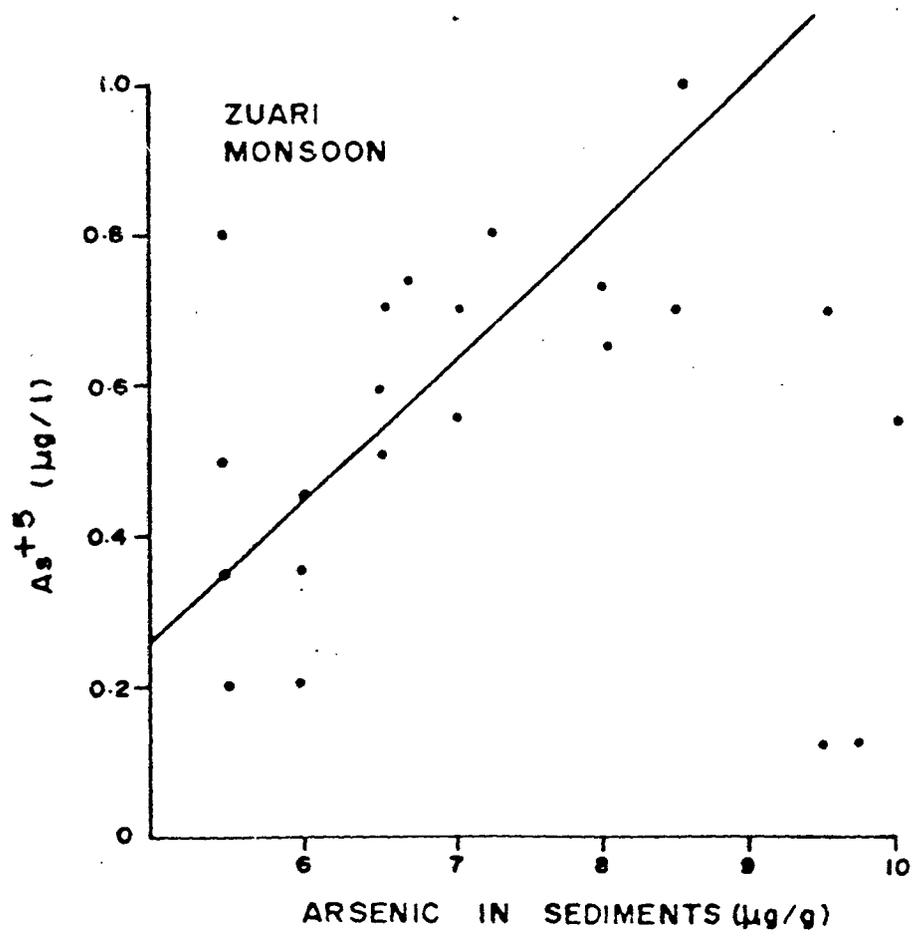


Fig.28

of arsenic in these sediments.

The plot of arsenate vs arsenic in sediment during the premonsoon and postmonsoon of both the estuaries did not reveal any significant trend, as there is appreciable scatter.

The element arsenic possess a tendency to become precipitated in the hydrolysates. It is enriched in oxidate sediments, chiefly by adsorption on ferric hydroxide. According to Goldschmidt and Peters (1934) the average content of arsenic in argillaceous sediments is of the same degree of magnitude as the average in igneous rocks. The analysis made by (Goldschmidt and Peters, 1934) shows an average of 4 g/ton arsenic in the sediment from the bottom of the Atlantic. Goldschmidt and Peters found that sedimentary siderite ores are materially low in the arsenic but the iron-rich bauxites and the glauconitic marine sediments are generally high in this element; which also follows iron in fresh water oxidates, however, manganese - rich oxidates are lower in arsenic. Hence the high values of arsenic found at station M-5 and M-6, Z-5 and Z-6 may be due to the above reason.

CHAPTER – VI

SUMMARY

VI SUMMARY

Arsenic may be introduced into the aquatic system through natural weathering and geothermal activity or via human activities such as mining and processing of ores.

This thesis records the results of the work done on the speciation of arsenic (arsenate and arsenite) in the Mandovi-Zauri estuarine system in Goa for a period of 14 months. In addition a few stations were covered along the west coast of India, and coastal areas of Mandovi and Zuari. Other allied parameters like dissolved oxygen, pH, salinity, silicate and phosphate were also studied. Sediment samples were analysed for total arsenic and organic carbon content.

Goa lies along the West coast of India. Both Mandovi and Zuari are coastal-plain estuaries of the drowned river valley type. They experience semi-diurnal tides and are influenced by seawater inflow round the year. During the non-monsoon months they are seawater dominated while during the monsoon these estuaries are

freshwater dominated; with the formation of salt wedge near the mouth. In the Mandovi estuary a sand bar formation is observed near the mouth during the monsoon. Zuari, on the other hand does not have any sand bar formation. The Mandovi-Zuari estuaries are the main waterways of Goa and are of utmost importance for the economy of the state as they flow through mining areas opening into the Arabian sea. About two-thirds of the total exploitation of iron, manganese and ferromanganese ores of Goa come from the mines located along the basins of these two rivers. They are mainly transported in barges through these estuaries to the harbour for export.

The results of the study are given below.

Salinity in these estuaries varied from 22.13 to 31.65×10^{-3} during premonsoon and from 0 to 9.05×10^{-3} during the monsoon and from 4.25 to 30.10×10^{-3} during the postmonsoon for the surface waters, while it varied from 22.19 to 30.23×10^{-3} , 0 to 24.32×10^{-3} and from 6.31 to 27.63×10^{-3} for the bottom waters of the Mandovi. Fluctuations of similar magnitudes were also observed for the Zuari estuary. Dissolved

oxygen was high throughout the estuary except during the monsoon period. The surface and bottom values did not show much difference in both these estuaries. The values at the upper reaches of the estuary were above 3.50 ml/l. During the premonsoon the oxygen concentration was the highest as compared to the other seasons. During premonsoon the photosynthetic productivity was high leading to increased oxygen production in these waters.

pH was higher during the premonsoon and lower during the monsoon. pH varied from 7.55 to 7.90 during the premonsoon and from 7.18 to 7.63, 7.66 to 8.08 during the monsoon and postmonsoon respectively for the surface waters. The pH values for the bottom was slightly higher at some of the stations. It varied from 7.53 to 7.86, 7.18 to 7.65, 7.60 to 8.06 for the bottom waters of the Mandovi. Similar trend was also observed in the Zuari. pH decreased towards the riverine end. Rainfall, river discharge, exchange from the sea are some of the important factors which influence pH variation in the estuarine waters.

Phosphate concentration was low during the premonsoon, but increased with the onset of monsoon. In the Mandovi estuary the phosphate concentration during the premonsoon varied from 0.53 to 1.15 $\mu\text{mol/l}$ for the surface and from 0.76 to 1.20 $\mu\text{mol/l}$ for the bottom waters. In the Zuari it ranged from 0.65 to 0.76 $\mu\text{mol/l}$ for the surface, while for the bottom it was 0.78 to 1.09 $\mu\text{mol/l}$. The low values recorded during the premonsoon might be due to diminished river discharge.

During the monsoon the values were high throughout the estuary, The surface values being higher than the bottom values. The surface values varied from 1.07 to 1.36, while it varied from 0.87 to 1.28 $\mu\text{mol/l}$ for the bottom waters of the Mandovi. In the Zuari the surface values varied from 1.77 to 2.26 $\mu\text{mol/l}$ while it varied from 1.72 to 2.04 $\mu\text{mol/l}$ for the bottom waters. The productivity in these estuaries is reported to show two peaks, one during the premonsoon and the second during the postmonsoon. Trichodesmium blooms have been reported at the mouth of the estuary. The high productivity is followed by a degradation of organic matter produced, which enhances the dissolution of some

elements including phosphorous. High concentrations observed at the mouth of the estuary may partly be due to degradation of organic matter. High phosphate concentration could be related to large amount of fertilizer used in agriculture during the monsoon. During the postmonsoon the phosphate concentration ranged from 0.85 to 1.27 $\mu\text{mol/l}$ for the surface and from 1.00 to 1.50 $\mu\text{mol/l}$ for the bottom waters of the Mandovi estuary. In Zuari it ranged from 0.59 to 1.10 $\mu\text{mol/l}$ and from 0.76 to 1.23 $\mu\text{mol/l}$ for the surface and bottom waters respectively.

Surface silicate varied from 6.79 to 54.04, 89.35 to 168.99, 22.13 to 126.40 $\mu\text{mol/l}$ during the premonsoon, monsoon and postmonsoon seasons respectively for the Mandovi. For the Zuari it varied from 5.62 to 80.53, 75.09 to 124.83 and 14.18 to 119.01 $\mu\text{mol/l}$ during the premonsoon, monsoon and postmonsoon respectively. Since silicon is mainly supplied by the river waters, its concentrations showed a decreasing trend from head to the mouth of the estuaries, due to dilution with sea water having low silicate concentrations and also due to utilization by plankton. During the monsoon higher

concentrations were observed throughout the entire length of the estuaries. It is also expected that during monsoon when rainfall and runoff was the highest the silicate content of river water should be higher. Silicates are concentrated more in the upper reaches and this is to be expected as it is of land origin, whereas in the outer reaches the concentrations are more or less similar to those in seawater. Mandovi had a higher concentration of silicate compared to Zuari, which may be due to the large number of streams draining into it.

Arsenate and arsenite show seasonal and spatial variations. During monsoon the arsenate and arsenite concentrations were higher compared to other seasons. During the monsoon arsenate concentrations varied from 0.40 to 0.78 $\mu\text{g}/\text{l}$ for the surface waters, while it varied from 0.34 to 0.79 for the bottom waters of the Mandovi. In the Zuari it varied from 0.45 to 0.79 at the surface and from 0.42 to 0.78 $\mu\text{g}/\text{l}$ at the bottom. Mining and shipping activities are known to contribute to the trace metals in the surrounding water column. During the monsoon concentrations of arsenate and arsenite were high as compared to the other seasons.

Theses 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 (as FeAsS) leaching into the river during the monsoon.

Analyses of As⁺⁵ and As⁺³ in iron ore, rainfall and sewage showed that a good amount of these are also added from these sources.

The waters of Mandovi and Zuari are very rich in dissolved iron and manganese because of the mining activities. Hydrolysis of iron (III) is one of the most likely reactions taking place when river water of pH 6-7 mixes with the seawater having a pH 8. Precipitation of iron have been reported by many workers. Coprecipitation with iron hydroxide could lead to a low concentration of arsenate at the high salinity region of the Mandovi and Zuari.

During the premonsoon arsenate concentration varied from 0.11 to 0.22 µg/l at the surface and from 0.13 to 0.27 µg/l for the bottom waters of the Mandovi. For the Zuari it varied from 0.13 to 0.20 and from 0.18 to 0.27

$\mu\text{g/l}$ for the bottom waters respectively. There was a gradual decrease in the arsenate concentration towards the lower reaches of the estuary. The decrease towards the mouth can be due to the mixing of the estuarine suspended matter of high metal content with marine suspension of low metal content. The concentration of arsenate and oxygen followed the same pattern low at the marine end and high at the fresh water end. The bottom values were high at the mouth of the estuary, but the concentration of arsenate was the highest upstream, which appears to be the effect of land drainage.

During the postmonsoon arsenate varied from 0.08 to 0.17 $\mu\text{g/l}$ for the surface waters and from 0.12 to 0.30 $\mu\text{g/l}$ for the bottom waters of Mandovi estuary. In the Zuari estuary it varied from 0.05 to 0.20 $\mu\text{g/l}$ for the surface and from 0.09 to 0.29 $\mu\text{g/l}$ for the bottom waters respectively. Postmonsoon values were more or less similar to the concentrations during premonsoon. According to Devassy (1983) Mandovi retains typical estuarine conditions for most part of the year with high phytoplankton counts, Chlorophyll a concentration and benthic production, while in Zuari the influence of sea

is more and consequently production is less. In Mandovi plankton analysis revealed a high level of arsenate. The concentration being higher at the mouth of the estuary which decreased gradually toward the upper reaches of the estuary. Zooplankton derives arsenic through phytoplankton which is known to extract this element as a nutrient having a biological function in seawater as a phosphate analogue (Johnson, 1972). Hence the high concentration of arsenate in Mandovi is due to high plankton or benthic production which solubilize metals.

Arsenite also showed seasonal and spatial variations in Mandovi and Zuari. However, the concentration of arsenite was at very low levels in both the estuaries. It varied from undetectable levels to 0.07 $\mu\text{g}/\text{l}$ for the surface waters and from undetectable levels to 0.10 $\mu\text{g}/\text{l}$ for the bottom waters of the Mandovi; while it varied from 0.04 to 0.11 for the surface waters and from 0.07 to 0.16 $\mu\text{g}/\text{l}$ for the bottom waters of the Zuari during the premonsoon. Surface and bottom waters of the Mandovi did not show any significant variation at most of the stations. In

unpolluted natural waters the occurrence of arsenite seems to be closely linked to primary productivity. Productivity is higher during premonsoon and occasional Trichodesmium blooms occur at the mouth of the estuary. Hence, the high values of arsenite at the mouth of the estuary is dependent on the phytoplankton population. Arsenate, the primary inorganic form of arsenic in oxidized natural waters, is highly reactive in productive estuaries, is taken up by phytoplankton and transformed into reduced forms and released into the water column.

During the monsoon the arsenite concentration was in elevated level throughout the estuaries. The values varied from 0.07 to 0.17 $\mu\text{g}/\text{l}$ for the surface and from 0.06 to 0.13 $\mu\text{g}/\text{l}$ for the bottom waters of the Mandovi. The arsenate values for Zuari varied from 0.06 to 0.19 $\mu\text{g}/\text{l}$ and from 0.09 to 0.16 $\mu\text{g}/\text{l}$ for the bottom waters respectively. The surface values being higher than the bottom waters of both the estuaries. At the freshwater region both the surface and bottom values were more or less of the same magnitude, the magnitude of the arsenite values being low compared to the values

obtained during the other seasons. Diatoms dominated the phytoplankton. Chaetoceros dominated among diatoms followed by Cyclotella and Skeletonema. These species may play an active role in producing arsenite and methylated arsenic compound also.

During the postmonsoon arsenite was found to be in very low concentrations in both the estuaries. It varied from 0.04 to 0.15 $\mu\text{g}/\text{l}$ for the surface, while it varied from 0.05 to 0.18 $\mu\text{g}/\text{l}$ for the bottom waters of the Mandovi. In Zuari it ranged from 0.02 to 0.06 $\mu\text{g}/\text{l}$ and from 0.03 to 0.09 $\mu\text{g}/\text{l}$ for the surface and bottom waters respectively. The arsenite values are not as high as during the premonsoon, the bottom values being higher than the surface values at almost all the stations in Mandovi and Zuari. The concentrations at the riverine and the marine end are low compared to the values at the intermediate stations. The postmonsoon months showed higher number of species of diatoms and dinoflagellates as well as cell counts (Devassy, 1983), which in turn can be related to the high concentration of arsenite in these estuaries. Thus the presence of

significant amounts of arsenite is governed by the amount of arsenate present in the estuarine system.

The estimation of the added or removed quantity of arsenate and arsenite showed variable trends. In general arsenate was removed from water. The major addition/removal patterns have been observed between 10 and 25×10^{-3} salinity in these estuaries.

The concentrations of arsenate and arsenite in the oceanic waters varied with depth. In the oxic zone arsenate is the most abundant form of arsenic. Arsenate is found to increase with depth. Except for a small amount of arsenite all the dissolved arsenic is in the arsenate form. Arsenite shows little variation with depth and appears to be regulated by the oxygen poor intermediate waters and associated chemical processes in the Arabian Sea. Average oceanic arsenic was observed as $2.5 \mu\text{g}/\text{l}$ in the Arabian Sea compared to $3 \mu\text{g}/\text{l}$ in oceans in general.

Arsenic concentration in the coastal waters showed wide variation. Arsenic concentration off Aguada varied from 0.06 to $0.22 \mu\text{g}/\text{l}$ for the surface, while for the

bottom it varied from 0.06 to 0.33 $\mu\text{g}/\text{l}$. Off Murmagao the arsenate concentration was slightly lower varying between 0.01 to 0.25 $\mu\text{g}/\text{l}$ and from 0.25 to 0.22 $\mu\text{g}/\text{l}$ respectively. Arsenite was at low levels or below the detection limit at most of the stations. The maximum concentration at the surface was 0.13 and for the bottom it was 0.14 $\mu\text{g}/\text{l}$ off Murmagao.

Arsenic in the estuarine sediment showed seasonal variations. The premonsoon season registering high arsenic from the marine end but decreases at the freshwater region. The concentration ranged from 5.84 to 8.94 $\mu\text{g}/\text{g}$ (dry wt) in the Mandovi while in Zuari it ranged from 5.07 to 10.20 $\mu\text{g}/\text{g}$ respectively. During the monsoon arsenic in the sediment of both the Mandovi and Zuari show the same trends with high values at the marine and the freshwater regions. Low values observed during the monsoon is due to the dilution by sea water. During the postmonsoon the arsenic concentration is higher throughout the estuary. Similar trend was also observed in the Zuari. The values ranged from 9.27 to 9.72 $\mu\text{g}/\text{g}$ and from 7.97 to 9.22 $\mu\text{g}/\text{g}$ for the Mandovi and Zuari respectively. The most probable source of arsenic

in these estuarine waters was considered to be from the dissolution of arsenic associated with iron ores.

Iron and manganese oxides are important components in regulating arsenic distribution in the sediments. In the Mandovi and Zuari estuarine sediments elevated levels of iron and manganese hydroxides have been reported at the freshwater regions which explains the high concentrations of arsenic observed there. freshwater stations. The precipitating manganese and ferric oxides entraps arsenic. Plankton readily extract trace metals from sea water. These organisms on decay settle to the bottom and the trace metal is released to the sediment by chelation and other processes.

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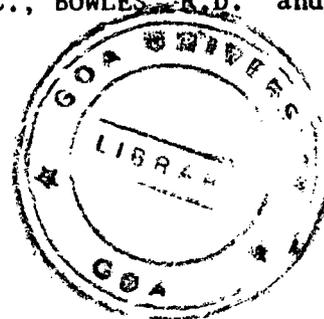
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