

Speciation and behaviour of Cd, Pb and Cu in Zuari estuary, west coast of India

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Received 21 September 1992; revised 24 May 1993

Dissolved labile and nonlabile forms of Cd, Pb and Cu in Zuari estuary measured for a period of 14 months showed lowest concentrations during the SW monsoon (June-Sept.) while maximum concentrations were observed during the premonsoon season (Feb.-May). Results of experiments conducted to evaluate the importance of desorption/dissolution revealed that the metal input due to desorption and dissolution of the particulate phase may not be very significant in the estuary.

An element or compound present in a natural water system will be distributed in a variety of physico-chemical states such as free ions, complexes or organo-metallic compounds or they may be adsorbed on to the particulate matter. All the different forms can co-exist and may or may not be in thermodynamic equilibrium with one another¹⁻³ and the distributions among these forms as well as the total concentrations vary between different environments¹.

Though several studies on different chemical aspects of Zuari have been made⁴⁻⁷, no attempt has so far been made to study the speciation and behaviour of important trace metals. Since the characteristics of the estuarine system are greatly influenced by the monsoonal cycle, a seasonal study is expected to shed light on the behaviour of metals during estuarine mixing. Such studies would also help to establish the background levels of the toxic metals in their different chemical forms for assessment of the extent of environmental pollution.

Dissolved metal by convention means that fraction of the metal which passes through a 0.45 μm membrane filter. In this study the dissolved metal is separated into 2 fractions only, the labile form and the nonlabile form. The labile fraction of the metal includes the metal ion plus the complexed metal which can dissociate very rapidly to the electro reducible form yielding an ASV (anodic stripping voltammetry) signal while the nonlabile metal is that fraction of the bound metal which becomes ASV labile when the organic matter in the sample is destroyed by U.V. oxidation.

Materials and Methods

Monthly observations were carried out from Feb. 1985 to March 1986 on the dissolved labile and nonlabile forms of Cd, Pb and Cu as well as the hydrographical parameters. The station positions are given in

Fig. 1. Observations from sts 1 to 6 were carried out once every month, sts 7 and 8 only twice, during each season. The values for the monsoon (June-Sept.) period at sts 1 and 8 are represented by the values for September only, as it was not possible to reach the stations during the monsoon months. Observations were carried out during low tide. Water samples were collected from 0.3 to 0.5 m below the surface to avoid contaminants. A precleaned 2 litre Niskin bottle on a nylon rope and a PVC coated messenger was used for collecting the sample. Sampling was done manually from the bow of a wood-hulled boat while it was moving very slowly, to avoid the risk of contamination from the boat. The samples for metals were transferred to precleaned⁸ polyethylene containers and filtered through membrane filter papers (0.45 μm). The first 500 ml was used for rinsing and the samples were stored⁹ at 4°C in precleaned polyethylene bottles at natural pH. The analyses of metals Cd, Pb and Cu were carried out by ASV¹⁰ in a laminar flow apparatus. Hydrography of the estuary and the particulate

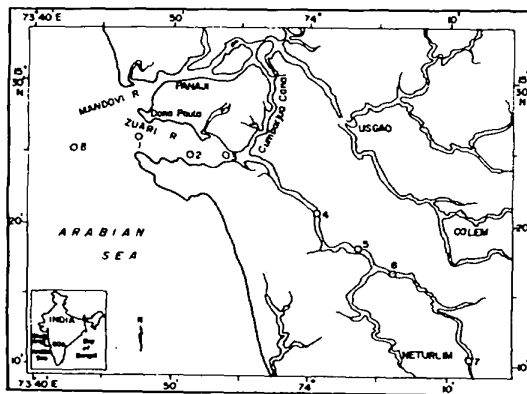


Fig. 1—Station locations

metal concentration have been dealt with elsewhere¹¹.

To evaluate the importance of desorption/dissolution in the estuary experiments were conducted similar to the one performed by Keeney-Kennicutt and Presley¹². Zuari river water (500 ml) was collected in April (in duplicate), filtered and suspended matter weight. The suspended matter (28.45 mg in each) with the filter was immediately transferred to two 100 g samples of unacidified, filtered Arabian Sea water collected the same day and shaken. One sample was filtered after 1 h and the other after 24 h. The filtrates and seawater blank were analysed for Cd, Pb and Cu by ASV¹⁰.

Results

Cadmium—Seasonal variations of labile and total

Cd are presented in Fig. 2. The highest concentration of Cd was during premonsoon (Feb.-May) period (Fig. 2A, D). Labile fraction of Cd varied from 0.03 to 0.15 $\mu\text{g.l}^{-1}$ while the total metal varied from 0.13 to 0.54 $\mu\text{g.l}^{-1}$. During monsoon (June-Sept.) the values reduced substantially. The labile Cd were in the range 0.02 to 0.06 $\mu\text{g.l}^{-1}$ while the total ranged between 0.04 and 0.14 $\mu\text{g.l}^{-1}$. The postmonsoon (Oct.-Jan.) values were slightly higher than the monsoon values in general. Nonlabile form during premonsoon fluctuated between 44 and 89% (Table 1), while during monsoon the values were between 17 and 66%. Postmonsoon values varied between 43 and 74%. In general Cd concentrations were higher at the mouth than the riverine (fresh water) side.

Lead—The behaviour of Pb was very similar to

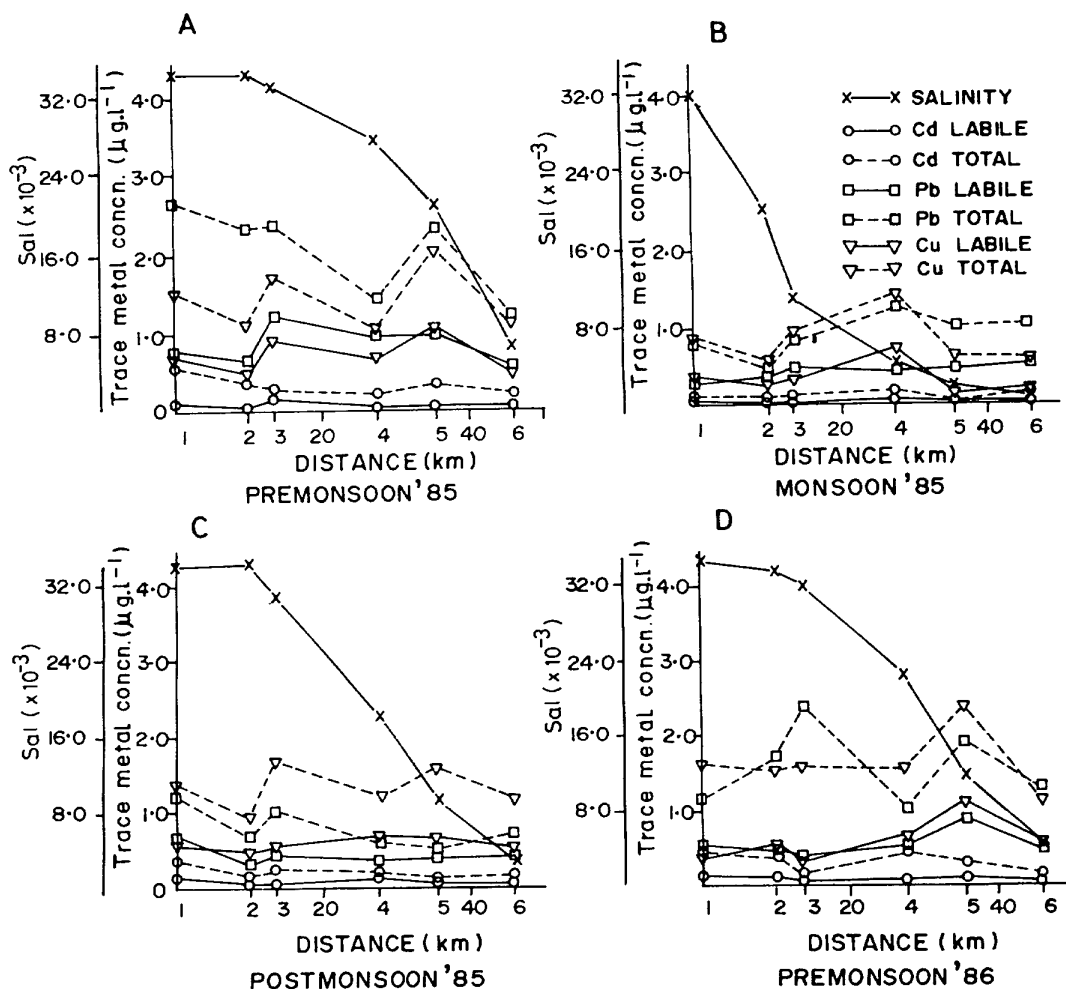


Fig. 2—Variations in labile and total concentrations of Cd, Pb and Cu during A = premonsoon (Feb.-May), B = monsoon (June-Sept.), C = postmonsoon (Oct.-Jan.), D = premonsoon (Feb.-March only).

Table 1.—Percentage of strongly complexed metals at Zuari estuary during Feb. 1985-March 1986

Station	Cd				Pb				Cu			
	A	B	C	D	A	B	C	D	A	B	C	D
1	81.5	50.0	51.5	75.0	82.5	65.1	40.2	74.3	79.6	60.5	54.3	75.8
2	82.9	16.7	58.8	75.0	73.3	16.7	47.9	69.2	56.6	50.0	49.0	64.9
3	44.4	50.0	73.9	53.3	48.1	40.0	51.0	84.2	45.7	66.4	64.9	78.3
4	81.0	57.1	42.9	79.1	30.4	65.4	44.0	43.9	82.7	50.0	46.3	56.5
5	88.9	50.0	55.6	74.2	52.4	56.9	24.0	53.2	47.4	62.0	56.6	53.7
6	85.0	65.7	55.2	76.5	50.4	50.0	38.7	61.4	56.4	67.2	56.8	50.9

A = Premonsoon (Feb.-May), B = Monsoon (June-Sept.), C = Postmonsoon (Oct.-Jan.), D = Premonsoon (Feb.-March only).

that of Cd (Fig. 2). During premonsoon (Fig. 2A, D) the values of labile Pb were in the range 0.38 to 1.25 $\mu\text{g.l}^{-1}$ while the total Pb varied between 0.98 and 2.66 $\mu\text{g.l}^{-1}$. Like other metals the concentration of Pb also decreased during monsoon. The labile concentration ranged between 0.29 and 0.52 $\mu\text{g.l}^{-1}$ and the total concentration varied from 0.42 to 1.30 $\mu\text{g.l}^{-1}$. During postmonsoon the values were in between those during monsoon and premonsoon. Nonlabile form varied between 30 and 84% during premonsoon while during monsoon the values were between 17 and 65% (Table 1). During postmonsoon the values were in the range 24 to 51%. During most of the period of observation, higher salinity regions had higher concentration of metals than the riverine station. Concentrations at sts 3 and 5 were higher compared to other stations. In general, waters nearer to the mouth regions had higher percentages of nonlabile form of Pb compared to the riverine side.

Copper—Cu also showed higher concentrations during premonsoon period (Fig. 2). Values of labile Cu during this period varied between 0.34 and 1.12 $\mu\text{g.l}^{-1}$ while those of nonlabile form were in the range 0.34 to 1.3 $\mu\text{g.l}^{-1}$. Total copper concentrations were in the range of 1.04 to 2.42 $\mu\text{g.l}^{-1}$. During monsoon concentration decreased substantially. Values during postmonsoon were intermediate. Percentage of nonlabile form were higher in premonsoon and lower during monsoon (Table 1). During both premonsoon and postmonsoon seasons the total concentration of the metal increased towards the mouth while the labile Cu decreased.

Discussion

In estuaries where river water and coastal or seawater of widely different composition mix, strong gradients in chemical and physico-chemical properties occur. There are contradictory reports in literature from various aquatic systems suggesting that trace metals are either adsorbed or desorbed in estuarine conditions. There can be a distinct seasonal vari-

ation or even diurnal variation within a particular estuary¹³⁻¹⁵. In the Zuari estuary there was a distinct seasonal fluctuation in the concentration of Cd, Pb and Cu. During monsoon the river discharge is much higher and the shipping activities are much less compared to other seasons. Because of the rough weather at the mouth of the estuary, loading of iron ore is at its minimum. Shipping and mining activities are known to contribute to trace metals and other pollutants in the environment^{15,16}. The dilution due to precipitation and reduced shipping and mining activities could have kept the concentration of all the metals at a lower level during monsoon season.

During premonsoon the conditions are different. A large number of barge transport iron and manganese ores through this estuary. There is little or negligible precipitation and river runoff is almost absent. As factors like light penetration and nutrient availability are favourable, the productivity is high during this season¹⁷. Occurrence of frequent blooms of *Trichodesmium* have been reported during this period in the Arabian Sea^{18,19}. Decaying *Trichodesmium* is known to release trace elements^{20,21}. Temperature is also higher during this period. High temperature kinetically favours decomposition²². The decomposition of organic matter releases the trace metals in the surface sediment which can be resuspended by tides and dredging²³⁻²⁵.

In addition to higher total metal concentration noticed during premonsoon, the percentage of nonlabile form was also higher during this period. There are evidences in the literature to show that the decomposition of phytoplankton brings nonlabile forms of the metals to the water column^{23,26,27}. Ostertroht *et al.*²⁸ argued that dissolved organic Cu exists in 2 forms, one probably originating mainly from humic acid like material, being responsible for the constant background level of dissolved organic copper, while the other was thought to have been formed from material produced recently by phytoplankton and micro organisms resulting in additional peak concentration of dis-

• Table 2 -Desorption of Cd, Pb and Cu from Zuari river suspended materials into seawater

		Cd (ppb)	Pb (ppb)	Cu (ppb)
Exchangeable metal concentration in suspended sediment	After 1 h	204 ± 33	489 ± 59	652 ± 62
	After 24 h	285 ± 47	733 ± 75	896 ± 83
Dissolved excess of observed on 22.4.88		0.31	1.52	0.96
Suspended sediment required to account for the observed excess	After 1 h	1.52 g.l ⁻¹	3.11 g.l ⁻¹	1.47 g.l ⁻¹
	After 24 h	1.09 g.l ⁻¹	2.07 g.l ⁻¹	1.07 g.l ⁻¹

solved organic Cu. Some others, for example, Jones *et al.*²¹ observed an increase in the labile form during *Trichodesmium* bloom period. They attributed this to the release of metal complexing material from senescent *Trichodesmium* and dissolution of metal ions adsorbed onto particulate material by this metal complexing matter. On the other hand this study showed an increase in nonlabile form during the bloom period. Probably the complexing material released from senescent *Trichodesmium* may be forming complexes either with the metal present in the dissolved phase in the water or with the metal released from bottom sediments.

A variable but systematic increase in the concentration of metals was observed towards the high salinity region. Chlorinity plays an important role in the adsorption/desorption character of a metal. Model calculations including the adsorbed fraction show that an increase in salinity causes a decrease in the adsorption²⁹. In addition to this, other mechanisms like ionic strength, pH, redox potential, microbiological activity, organic matter degradation and the residence time of the particle in the mixing zone also play an important role³⁰. The water of Zuari is very rich in dissolved Fe and Mn because of the mining activities³¹. When river water of typical pH 6-7 mixes with the seawater of pH 8.1 hydrolysis of Fe(III) is one of the most likely reaction. Precipitation of Fe has been reported by many workers^{32,33}. Co-precipitation with the iron hydroxide could have led to a decrease in the concentration of Cd, Pb and Cu towards the high salinity region. If the release of metal from bottom sediment pore waters was significant during the observation period, it may probably have obscured the effects of processes resulting in removal of metals from solution into particulate matter during estuarine mixing as observed in the Rhine estuary³⁴⁻³⁶.

From the experiments conducted to evaluate the importance of desorption/dissolution, the exchanged metal concentration in the suspended sediment was calculated by:

$$\text{Exchangeable metal concentration in the sediment (ppb)} = \frac{\text{Experimental net increase in the solution (ppb)}}{\text{Solution wt. (g)}} \times \frac{\text{Solution wt. (g)}}{\text{Sediment wt. (g)}}$$

Maximum dissolved trace metal increase in the river was estimated by constructing a theoretical dilution line between the seawater end member and the dissolved metal concentration in river water end member and calculating the excess. The sediment load required to account for the dissolved excess metal concentration if desorption/dissolution were the only mechanisms was determined by:

$$\text{Sediment load (g.l}^{-1}\text{)} = 10 \times \frac{\text{Dissolved metal excess (ppb)}}{\text{Exchangeable metal concentration of the sediment (ppb)}}$$

To explain the observed dissolved metal excess, the sediment load required was 1.09 to 1.52 g.l⁻¹ for Cd (Table 2) if desorption/dissolution were the only processes responsible for the higher concentration at the mouth, that day. But during the day of observation the suspended matter was only 19.6 mg.l⁻¹. Moreover, the maximum observed suspended matter concentration during the whole observation period was 82 mg.l⁻¹. Similar experiments for Pb and Cu yielded values between 2.07 and 3.11 and 1.07 and 1.47 g.l⁻¹. Hence desorption/dissolution process cannot explain the high dissolved trace metal concentration at the river mouth. Hence it can reasonably be assumed that the other processes, viz. the remobilisation of metals^{12,37} and the contribution from dredging and shipping activities are the main reasons for the higher concentration of metals at the mouth. As discussed earlier the higher productivity and subsequent decay¹⁷⁻¹⁹ also contribute to seasonal higher concentration at the mouth. This is supported by the fact that the phosphate profile¹¹ also showed increase towards the high salinity region. Other workers^{38,39} also found similar relationship with phosphate.

Acknowledgement

Author is grateful to Dr R Sen Gupta for valuable advice and critical review, and Dr B N Desai, Director for his keen interest in the work.

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