

Determination of Cd, Pb & Cu in Mandovi Estuary by Differential Pulse Anodic Stripping Voltammetry

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Dissolved labile and non-labile (organically associated) concentrations of Cd, Pb and Cu in Mandovi estuary have been measured for 1 y (Feb. 1980 to Jan. 1981). Percentage non-labile form varies from 0-50% of the total for Cd, from 0-60% for Pb and 0-80% for Cu. Compared to the reported values from other estuaries, Mandovi estuarine waters have registered a higher concentration of the metals. These high concentrations, to a large extent, are considered to be the effect of the leachings from the near about mining zone and transportation of the ores by barges in this estuary.

Several metals dissolved in seawater may be present in a number of different chemical forms^{1,2} and their behaviour in the marine environment depends on their physico-chemical form. For example, (i) the toxicity and availability to organisms are related to particular metal species rather than to total metal concentration^{3,4}, and (ii) rate of a chemical process in which the element takes part and adsorption-desorption processes are influenced by the forms of the metal⁵⁻⁷. The presence of organically associated forms of metals in sea, estuarine and riverine water has been reported^{1,8,9}.

In the Mandovi estuary (lat. 15°31' N; long. 73°45' E) very few studies have been made and they deal mainly with Cu^{11,12}. The present paper reports the results of the study of labile and non-labile forms of Cd, Pb and Cu in the dissolved state as the dissolved state is considered to be the most important transfer stage of toxic metals¹³.

Materials and Methods

In the present study the dissolved metal is separated into 2 fractions only, anodic stripping voltammetry (ASV) labile and ASV non-labile. The labile fraction of the metal includes the metal ions plus complexed metal which can dissociate very rapidly to the electro-reducible form yielding an ASV signal¹⁰ while the non-labile metal is that fraction of the bound metal which becomes ASV labile when the sample is UV oxidised.

Three stations were chosen (Fig.1) along the Mandovi river and monthly samples were collected during Feb.1980 to Jan.1981. Surface seawater samples were collected from approx. 20cm below surface to avoid contaminants. Pre-cleaned Niskin Bottles were used for surface and bottom water sampling. Observations were made on the same day

starting from st A and ending at st C. The samples were stored prior to filtration in polyethylene carbuoys (5 l) pre-cleaned with 6 M HCl and conditioned for 1 week in artificial seawater made from ultra pure chemicals¹⁴. Filtration was carried out using millipore membrane filter paper (0.45µm) previously rinsed with HCl and washed with deionised and double distilled water. The filtered samples were stored at 4°C in pre-cleaned polyethylene bottles. All samples were analysed within a week of the collection. Before the analysis, the samples were allowed to attain room temperature (23-25°C). Each sample was divided into 2 portions. One portion was analysed¹⁵ directly for the labile metal at natural pH. The other portion was transferred to clean quartz tubes, 2 drops of H₂O₂ added and oxidised by exposing the sample to UV light for 3-4 h in a UV photooxidation unit (La Jolla Scientific Company, California). After oxidation, when the samples attained room temperature, they were analysed for total metal. The non-labile metal was found by difference.

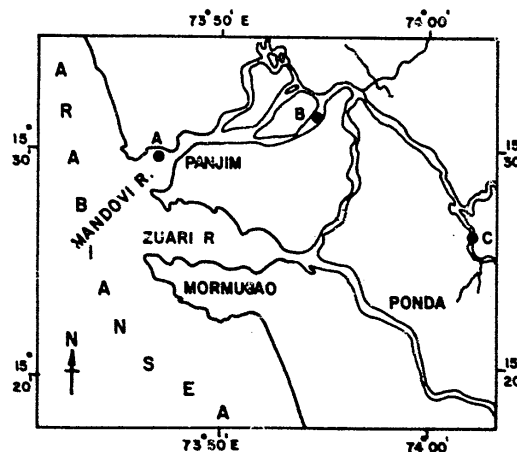


Fig. 1—Station locations

* Deceased.

The analysis was carried out by anodic stripping voltammetry in differential pulse mode on a EG & G PARC polarographic analyser (Model 174 A) combined with an automated electroanalysis controller (Model 315 A) and a static mercury drop electrode (Model 303). The polarogram was recorded using Houston Instruments Omnigraphic 2000 X-Y recorder. A constant rate magnetic stirrer (Model PAR 305) and a teflon coated bar was used for stirring. Working electrode was a hanging mercury drop electrode (HMDE). The glass capillary was siliconised with 5% dichlorodimethyl silane. Reference electrode was Ag/AgCl. A platinum wire acted as counter electrode. The samples were taken in teflon cell bottoms. Dissolved oxygen was removed from the samples by purging nitrogen gas for 10 min and surface of the sample was blanketed by nitrogen during the experiment. The dissolved oxygen in the purging gas was removed by passing the gas through vanadous chloride solution and saturated with moisture by passing through the same solution used for conditioning the sampling bottles in order to avoid evaporation of the test solution. The deposition was carried out for 15 min at -0.8 V with stirring of the solution. A pulse amplitude of 25 mV and current sensitivity of $10 \mu\text{A}$ was used. Drop time was 0.5 sec. After deposition, the sample was equilibrated for 30 sec and was scanned from -0.8 to 0 V at a rate of $2 \text{ mV} \cdot \text{sec}^{-1}$. The concentration was calculated by standard addition of the metal to the UV oxidised portion of the respective sample deaerating it to a further 5 min. Eppendorf micropipettes were used for standard addition after washing the pipette tips with acid and water. Peak area was calculated as the product of peak height and width at half height. The area obtained by this method was shown to be very similar to area obtained by direct measurement even when peaks were broad and somewhat unsymmetrical in shape¹⁶. Deionised and double quartz distilled water was used for washing and making reagents. The working standard was prepared daily. Standard deviation was found to be 14, 18 and 12% respectively for Cd, Pb and Cu. Salinity estimation was done by titration and pH was read on an Orion Research pH/ion meter. Surface seawater temperature was noted.

Results and Discussion

St A—The depth of the station was 11 m. Surface salinity was more than 31×10^{-3} except in monsoon (June to Sept.) when it reached a low value (0.54×10^{-3}). Bottom salinity was very much higher in monsoon than the surface salinity. In Dec. an exceptionally high value of 40.97×10^{-3} was observed. Temperature variations were typical of the inshore waters

Variations in concentration of the dissolved labile and non-labile Cd, Pb and Cu are presented in Fig. 2. Pronounced maximum values for all metals both at surface and bottom were observed in Sept. except for non-labile form of Cd which showed very low values. These high concentrations, particularly at the bottom, might be due to the proximity of bottom waters to the mud water interface. During Dec. very high concentration of labile Cd was observed, which is associated with very high surface salinity. Low values of non-labile form suggest that the origin of the high labile Cd may be from other sources, possibly from ships and industry¹⁸. In fact, shipping activity is considerable in this river and the sewage outlet point of Panaji city is not far from st A.

Concentration of labile Pb varied from 0.28 to $10 \mu\text{g} \cdot \text{l}^{-1}$ except in Nov. and Jan. In Nov. high concentration of labile Pb was observed but the non-labile form was non-detectable suggesting human activity as the possible cause¹⁸. But in Jan. the concentrations of both the labile and non-labile forms were higher with possible transformation of the labile into non-labile form. The Cu concentrations were very high during Sept.-Nov., both at the surface and bottom. In Dec. the measurement could not be made for Cu because of some persisting unknown interference.

St B—The water depth was about 8 m. Temperature varied from 26°C in Aug. to 33.5°C in April while the salinity varied from 0.1×10^{-3} in Aug. (monsoon) to 33×10^{-3} in May.

Labile Cd concentration varied between 0.05 and $1 \mu\text{g} \cdot \text{l}^{-1}$ except in Feb. and Dec. (Fig. 3). The peak value of Cd in Feb. was associated with high values of Pb and Cu. In Dec. though Cd value was very high, it was much lower than that at st A. The high concentration at this station might be due to movement of the high cadmium water at st A with the tide. The high labile Pb value both at surface and bottom was associated with very low salinity (0.1×10^{-3}) suggesting the land runoff as a possible cause. The non-labile form of Pb varied from 0 to $3 \mu\text{g} \cdot \text{l}^{-1}$ except in Feb.

There are 2 maxima for labile Cu, one in Feb. and another in Oct. The February maximum is accompanied by similar one for Pb and Cd whereas in Oct. only Cu has a high concentration. In Feb. the concentration of non-labile form also was high, while in Oct. it was very low (Fig. 3). The copper concentrations were consistently higher, perhaps due to the leachings from the mines situated along both the sides of the river. Such high values due to mining activities were reported earlier^{19,20}.

St C—As the station was very shallow (1-2 m), only surface samples were collected. The station for most of

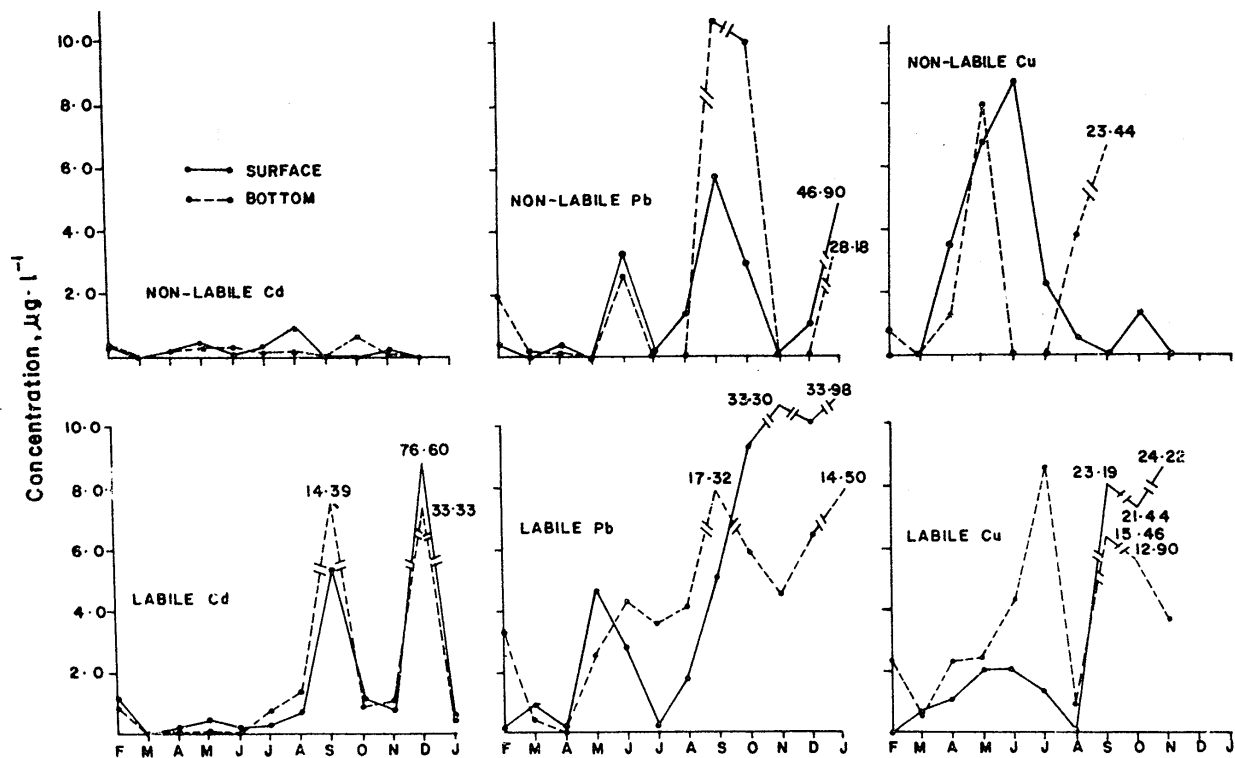


Fig. 2—Variations of dissolved labile and non-labile concentrations of Cd, Pb and Cu at st A.

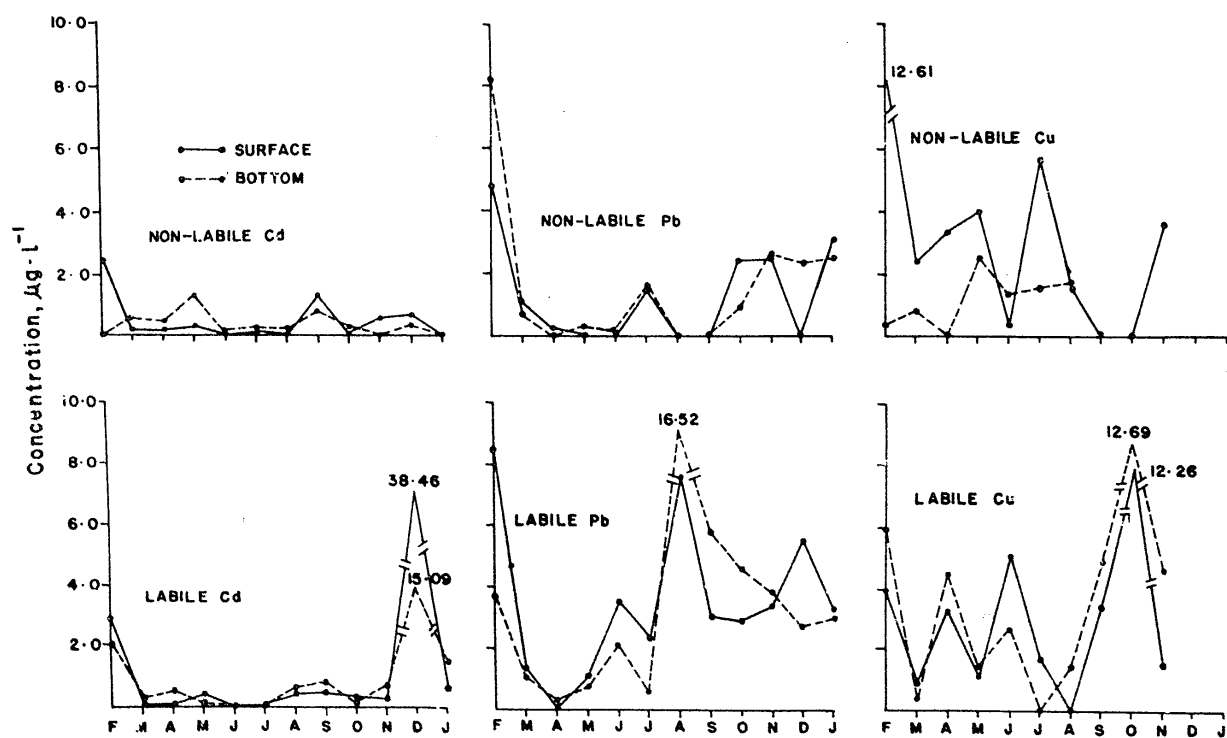


Fig. 3—Variations of dissolved labile and non-labile concentrations of Cd, Pb and Cu at st B.

the time has no influence of seawater. In monsoon and postmonsoon period the salinity was almost zero. The highest salinity (11.02×10^{-3}) was in April and May. Compared to other 2 stations the concentrations of all the 3 metals are much less (Fig. 4). This could be probably because there is no shipping activity in this region. Similar observations were reported by Mart *et al.*²¹. The high value of labile Cd observed in Dec. shows the influence of high Cd content water from st A. In addition to this high value, a simultaneous maxima of all the 3 metals (labile form) were observed in May.

The characteristics of different estuarine systems will vary with the nature of fresh water input and sediment characteristics⁹. Breder *et al.*²² found that ionic concentrations of trace metals were roughly inversely related to salinity while Abdulla and Royle²³ reported decrease in total dissolved Zn, Cu and Cd concentrations with increasing salinity. From the present data no such trends were evident as also observed earlier⁹.

The present data are in agreement with those reported by Fukai and Huynh-Ngoc¹⁸ that the appearance of local high value for one metal does not necessarily represent high values for other metals although certain simultaneous maxima of all the metals were observed during the period. Many times, sharp fall of these high values was noticed during the next observation. These types of differences in the metal content within a few days interval are difficult to explain satisfactorily from the present data. These variations may be due to different processes such as freshwater runoff, temporary pollution¹⁸, physico-chemical reactions like adsorption and desorption by suspended particulate material²⁴, etc. or a combined effect of some or all of these processes.

The spatial variation of the metal definitely shows a distinct trend. In the premonsoon period (Feb.-May), when there is little addition of fresh water the concentration of all the metals decreases from the riverine section towards the mouth of the estuary, showing general river water characteristics²⁵. With the onset of monsoon (June-Sept) the trend is reversed. The concentration of all metals decreases from the mouth towards the upper reaches of the estuary. The trend is continued in the postmonsoon (Oct.-Jan.) also. The input of the metals which is expected to be high in monsoon period might have been affected by the increased load of suspended matter, causing adsorption of the metals in the freshwater zone and gradually released at higher salinities reaching maximum near the mouth. Turekian²⁶ observed that the adsorbed form of metals in streams and rivers are always released to a greater or lesser extent on contact

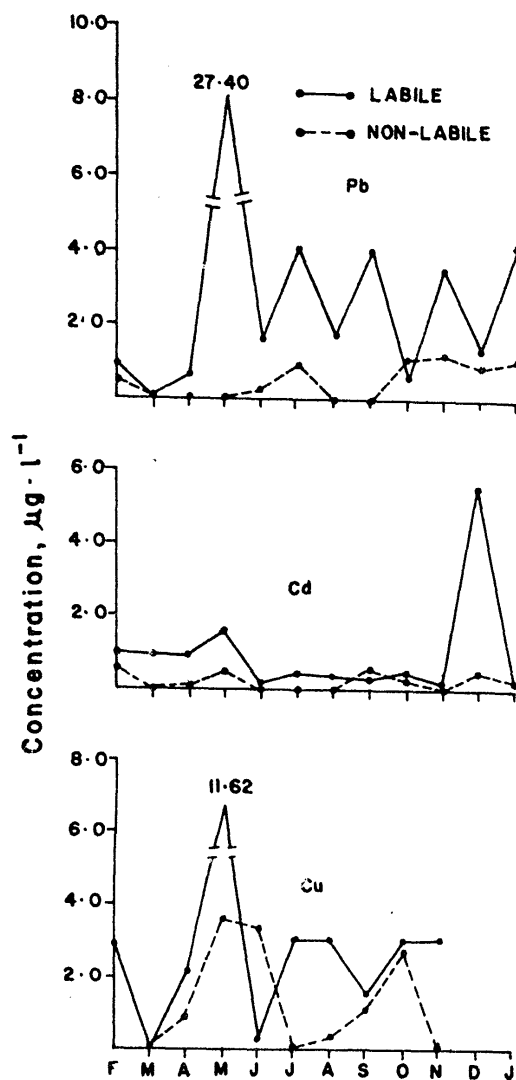


Fig. 4— Variations of dissolved labile and non-labile concentrations of Cd, Pb and Cu at st C.

with seawater due to their displacement by major ions like Mg and Na present in seawater.

In general, the concentrations of all the metals are lower in monsoon than in pre-monsoon and post-monsoon. This is probably because of the less contribution of the metal from barges which transport¹⁹ iron and manganese ores to the ships stationed outside the barmouth. During monsoons, the Mandovi river is closed for traffic because of sand bar formation in the mouth of the estuary. The lower concentrations in monsoon could also be due to the scavenging action of the suspended matter which is high in monsoon. Similar observations of low concentrations in water rich in suspended matter has been reported^{12,21}.

Compared to the reported values^{9,22} from other estuaries, the Mandovi estuarine water contains a higher concentration of dissolved metals. This is

probably because the leaches from the mines situated at both sides of the river find their way into the river. The runoff from the mineralised zones and sites of mining activity can be the source for trace metals²⁰. There may be substantial contribution from barge traffic also^{19,21}.

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References

- 1 Batley G E & Florence T M, *Mar Chem*, **4** (1976) 347.
- 2 Alexander J F & Corcoran E F, *Limnol Oceanogr*, **12** (1967) 236.
- 3 Allen H E, Hall R H & Brisbin T D, *Environ Sci Technol*, **14** (1980) 441.
- 4 Pagenkopt G K, Russo R C & Thursten R V, *J Fish Res Bd Can*, **31** (1974) 462.
- 5 Pytkowicz R M, *J Geol*, **73** (1965) 196.
- 6 Pytkowicz R M, *Am Sci*, **273** (1973) 515.
- 7 O'Connor T P & Kester D R, *Geochim Cosmochim Acta*, **39** (1975) 1531.
- 8 Nürnberg H W & Valenta P, in *Nature of sea water*, edited by E D Goldberg (Dahlem Workshop Report, Berlin) 1975, 87.
- 9 Batley G E & Gardner D, *Estuar Coast Mar Sci*, **7** (1978) 59.
- 10 Paul F & Bruce M, *Anal Chem*, **52** (1980) 1333.
- 11 Sankaranarayanan V N & Reddy C V G, *Curr Sci*, **42** (1973) 223.
- 12 George M D & Sawkar K, *Mahasagar—Bull Natn Inst Oceanogr*, **14** (1981) 71.
- 13 Nürnberg H W & Raspor B, *Environ Tech Lett*, **2** (1981) 457.
- 14 Nürnberg H W, Valenta P, Mart L, Raspor B & Sipos L, *Fresenius Z Anal Chem*, **282** (1976) 357.
- 15 Lund W & Onshus D, *Anal Chim Acta*, **86** (1976) 109.
- 16 Gardiner J & Stiff M J, *Water Res*, **9** (1975) 517.
- 17 Morris A W, *Mar Poll Bull*, **5** (1974) 54.
- 18 Fukai R & Huynh-Ngoc L, *Mar Poll Bull*, **7** (1976) 9.
- 19 Valenta P, Nürnberg H W, Khahre R, Merks A G A, Reddy S J & Rutzel H. A comparative study of toxic trace metals in the estuaries of the Ooster and Wester Scheldt and of Seirra Leone river. Paper presented at seminar on Estuaries—Their physics, chemistry, biology, geology and engineering aspects, 7-11 Dec. 1981, NIO, Goa, India.
- 20 Abdullah M I, Royle L G & Morris A W, *Nature Lond*, **235** (1972) 158.
- 21 Mart L, Nürnberg H W, Valenta P & Stoeppler M, *Thalassia Jugoslavica*, **14** (1978) 171.
- 22 Breder R, Nürnberg H W & Stoeppler M, *Ves Journees Etud Pollutions, Cagliari*, CIESM (1980) 285.
- 23 Abdulla M I & Royle L G, *J Mar Biol Ass UK*, **54** (1974) 581.
- 24 Kharkar D P, Turekian K K & Bertine K K, *Geochim Cosmochim Acta*, **32** (1968) 295.
- 25 Riley J P & Chester R, *Introduction to marine chemistry* (Academic Press, London) 1971, 465.
- 26 Turekian K K, in *Impingement of men on the oceans*, edited by D W Hood (Wiley Interscience, New York) 1971, 9.