



IMPACT OF ACIDIFICATION ON HEAVY METAL POLLUTION IN HOOGLHY ESTUARY

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Abstract

The surface water pH, dissolved heavy metals (Zn, Cu, Pb) and biologically available heavy metals (Zn, Cu, Pb) in the surface sediment were monitored for 30 years in the Hooghly estuary located in the western sector of Indian Sundarbans. The gradual decrease of surface water pH played a significant role in the process of compartmentation of heavy metals in the estuarine system. It is observed that lowering of pH triggered the process of transference of heavy metals from the sediment to the overlying aqueous system. The correlation coefficient values and scatter plots support our findings. Such phenomenon is of considerable importance while developing the management action plan to control heavy metal pollution in the estuarine system.

Keywords: Acidification, Surface water pH, dissolved heavy metals, biologically available heavy metals in the sediment.

Introduction

Ocean acidification has become an important topic of research in recent times. The change in pH of the aquatic phase is a reflection of the rate of acidification. The pH of sea water, which is ~8.20, is largely a function of the dissociation of the dissolved inorganic carbon (DIC), whose relative proportions by mass are ~0.5% aqueous carbon dioxide (CO₂), ~89% bicarbonate (HCO₃⁻)

and ~11% carbonate (CO₃⁻²). In the ocean water, these components together form ~2200 μmol/kg. Acidification of seawater is caused when the rate of increase in carbon dioxide exceeds the rate at which weathering, transport and mixing processes can deliver HCO₃⁻ and CO₃⁻² to buffer against the increased carbonic acid (H₂CO₃). The process of acidification largely regulates the concentration of conservative pollutants (primarily heavy metals) in the water and sediments. It has been documented by several researchers that aquatic pH controls the process of dissolution / precipitation and there by regulates the level of heavy metals in the aquatic phase and the underlying sediment compartments¹⁻⁵. The present paper is an attempt

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to find the role of acidification of estuarine water of Indian Sundarbans on the concentration of zinc (Zn), copper (Cu) and lead (Pb) in the ambient media. We have taken up this programme with the background of gradual increase of carbon dioxide in the Indian atmosphere and subsequent decrease of pH in the estuaries of Indian Sundarbans⁶.

Materials and Methods

Study Area

Indian Sundarbans at the apex of Bay of Bengal is noted for its rich mangrove diversity. The delta is comprised of 102 islands and the present study was undertaken in a sampling station 2.8 km off Namkhana island (21°76'67.00"N/88°23'33.00"E) in the western part of the delta. The island receives the freshwater input through the Hooghly River, which also contains discharges from several factories and industries located around the bank of the river^{7,8}.

Measurement of aquatic pH

pH of the surface water in the selected sampling station was measured during high tide condition with a portable pH meter (sensitivity = ± 0.02).

Analysis of dissolved Zn, Cu and Pb

Surface water samples were collected using 10-l Teflon-lined Go-Flo bottles, fitted with Teflon taps and deployed on a rosette or on Kevlar line, with additional surface sampling carried out by hand. Shortly after collection, samples were filtered through Nuclepore filters (0.4 μm pore diameter) and aliquots of the filters were acidified with sub-boiling distilled nitric acid to a pH of about 2 and stored in cleaned low-density polyethylene bottles. Dissolved heavy metals were separated and pre-concentrated from the seawater using dithiocarbamate complexation and subsequent extraction into Freon TF, followed by back extraction into HNO_3 as per the procedure of Danielsson *et al* (1978)⁹. Extracts were analyzed for Zn, Cu and Pb by Atomic Absorption Spectrophotometer (Perkin Elmer: Model 3030). The accuracy of the dissolved heavy metal determinations is indicated by good agreement between our values and reported for certified reference seawater materials (CASS 2) (Table 1a).

Table 1a – Analysis of reference material for near shore seawater (CASS 2)

Element	Certified value ($\mu\text{g l}^{-1}$)	Laboratory results ($\mu\text{g l}^{-1}$)
Zn	1.97 ± 0.12	2.01 ± 0.14
Cu	0.675 ± 0.039	0.786 ± 0.058
Pb	0.019 ± 0.006	0.029 ± 0.009

Analysis of biologically available Zn, Cu and Pb

Sediment samples from surface (1 cm depth) were collected by scraping using a pre-cleaned and acid washed plastic scale and immediately kept in clean polythene bags, which were sealed. The samples were washed with metal free double distilled water and dried in an oven at 105°C for 5 – 6 hours, freed from visible shells or shell fragments, ground to powder in a mortar and stored in acid washed polythene bags. Analyses of biologically available metals were done after re-drying the samples, from which 1 gm was taken and digested with 0.5 (N) HCl as per the standard procedure outlined by Malo (1977)¹⁰. The resulting solutions were then stored in polythene containers for analysis. The solutions were finally aspirated in the flame Atomic Absorption Spectrophotometer (Perkin Elmer: Model 3030) for the determination of metal concentrations. No detectable trace metals were found in the reagent blank. Analysis of the NIES Sargasso sample was carried out to assure the quality of the data (Table 1b).

Table 1b – Analysis of reference material (NIES Sargasso sample) for sediments obtained from the National Institute of Environmental Studies, Japan

Element	Certified value ($\mu\text{g g}^{-1}$)	Laboratory results ($\mu\text{g g}^{-1}$)
Zn	28.6	26.2
Cu	14.9	13.7
Pb	2.4	2.9

Statistical Analysis

Inter-relationships between aquatic pH, selected dissolved heavy metals and biologically available heavy metals in sediment were determined through correlation coefficient values, scatter plots and allometric equations for all possible combinations. All statistical calculations were performed with SPSS 9.0 for Windows.

Results

1. Surface water pH

The surface water pH exhibited variation within a small range. Highest value was recorded during 1984 (8.34) and lowest value (8.27) was recorded during 2013 (Fig. 1). The gradual lowering of pH ($2.3 \times 10^{-3}/\text{yr}$) clearly confirms the phenomenon of acidification of estuarine water in the study area.

2. Dissolved metal

The order of dissolved heavy metals in the estuarine water is $\text{Zn} > \text{Cu} > \text{Pb}$. Dissolved Zn ranged from 234.29 ppb during (1984) to 501.90 ppb during (2013) (Fig. 2). Dissolved Cu ranged from 50.95 ppb during (1984) to 264.00 ppb during (2013) (Fig. 3). During the study period the value of dissolved Pb ranged from 8.59 ppb (1984) to 43.83 ppb (2013) (Fig. 4).

3. Sediment metal

In sediment compartment, the temporal variation of biologically available metals exhibited a decreasing trend. In case of Zn, the value ranged from 42.44 ppm (during 2013) to 92.75 ppm (during 1984) (Fig. 5). In case of Cu the value ranged from 12.05 ppm (during 2013) to 32.49 ppm (during 1985) (Fig. 6). In case of Pb the lowest value was observed during 2013 (3.88 ppm) and the highest value was recorded during 1985 (20.47 ppm) (Fig. 7). It is also noted that the order of biologically available heavy metals in sediment is similar to that of dissolved heavy metals ($\text{Zn} > \text{Cu} > \text{Pb}$).

Discussion

The increase of atmospheric carbon dioxide in West Bengal, a maritime state in northeast coast of India has touched almost 51% since 1980¹¹. The gradual increase of carbon dioxide coupled with unplanned expansion of shrimp culture,

urbanization and industrialization has lowered the aquatic pH considerably⁶. The process has significantly increased the rate of dissolution of precipitated heavy metals from the sediment compartment to the water column and altered the speciation of selected heavy metals in the study area. The phenomenon of chemical speciation is governed by a number of factors like distribution, mobility, biological availability of chemical elements (it's chemical or physical association), pH, redox potential and availability of reactive species such as complexing ligands (organic and inorganic), particle surface for adsorption and colloidal matter. In the present study, such in-depth effort has not been attempted, but significant negative correlations between aquatic pH and dissolved heavy metals and significant positive correlations between aquatic pH and biologically available heavy metals in sediment (Table 2) confirm the role of pH as one of the key factors influencing chemical speciation of the heavy metals in the present geographical locale. The scatter plots (Fig. 8 -13) explain the significant negative and positive relationships of aquatic pH with dissolved and biologically available heavy metals in surface sediments respectively. The present study is in accordance with the earlier works in this area¹², which was conducted in short term temporal scale. A consequence of ocean acidification is a decreased concentration of OH^- and CO_3^{2-} . These anions form strong complexes in ocean water with divalent and trivalent metals¹³ and such reduction is expected to change the speciation of numerous metal ions in seawater¹⁴. To our knowledge, this is the first study to evaluate the impact of acidification on the heavy metal level in the ambient media of Sundarban water, which confirms the regulatory role of gradual acidification of estuarine water on Zn, Cu, and Pb concentrations in the aquatic phase and underlying sediment compartment of the present deltaic complex. The present study suggests the inclusion of acidification phenomenon of coastal water while formulating management action plan to reduce heavy metal pollution in the estuarine system.

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Table 2– Inter-relationships between pH, dissolved heavy metals and biologically available heavy metals in sediment

Combination	r value	p value
pH × dissolved Zn	-0.87907	<0.01
pH × dissolved Cu	-0.93591	<0.01
pH × dissolved Pb	-0.93164	<0.01
pH × sediment Zn	0.967428	<0.01
pH × sediment Cu	0.875562	<0.01
pH × sediment Pb	0.945385	<0.01

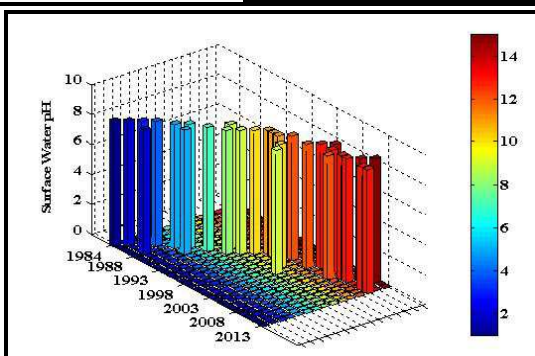


Fig. 1. Temporal variation of surface water pH in the study site

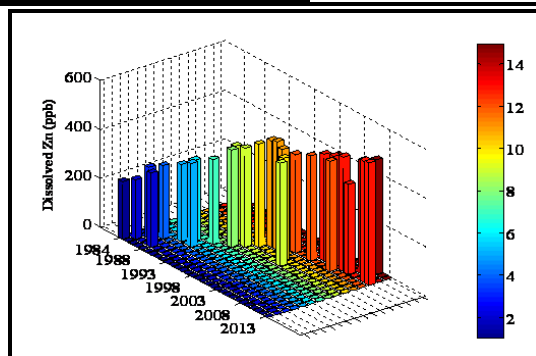


Fig. 2. Temporal variation of dissolved Zn (ppb) in the study site

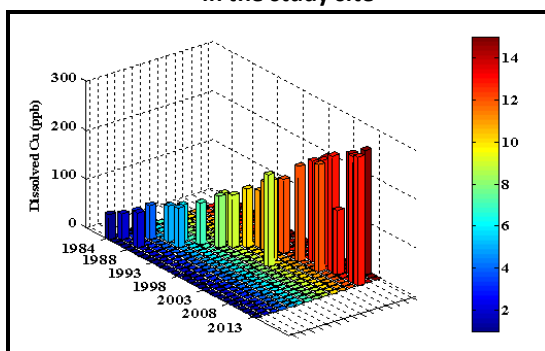


Fig. 3. Temporal variation of dissolved Cu (ppb) in the study site

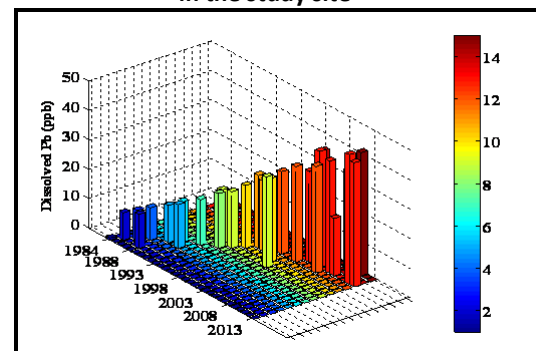


Fig. 4. Temporal variation of dissolved Pb (ppb) in the study site

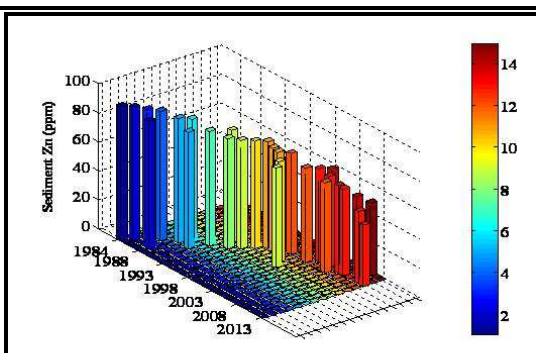


Fig. 5. Temporal variation of sediment Zn (ppm) in the study site

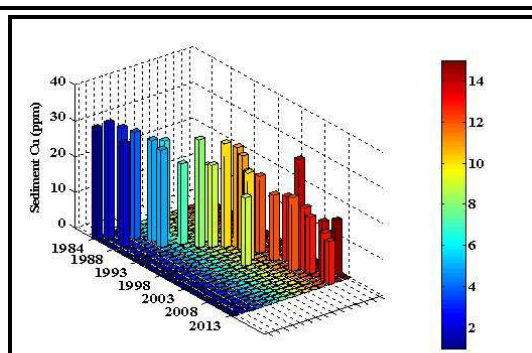


Fig. 6. Temporal variation of sediment Cu (ppm) in the study site

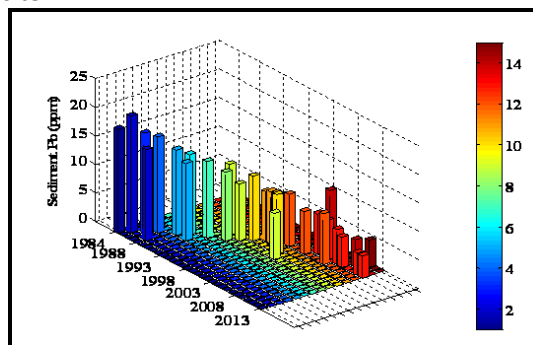


Fig. 7. Temporal variation of sediment Pb (ppm) in the study site

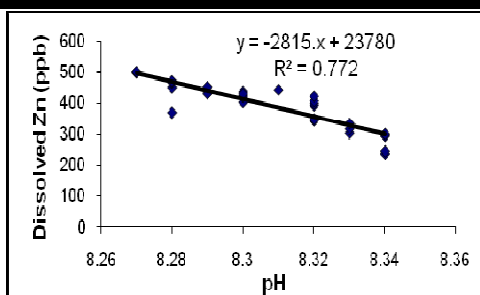


Fig.8. Inter-relationship between dissolved Zn and pH

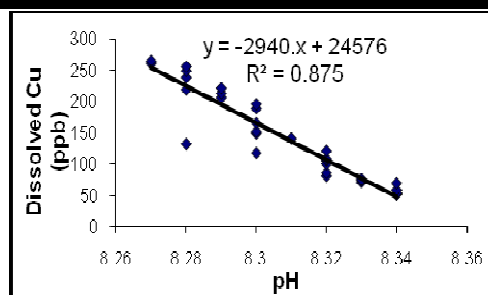


Fig. 9. Inter-relationship between dissolved Cu and pH

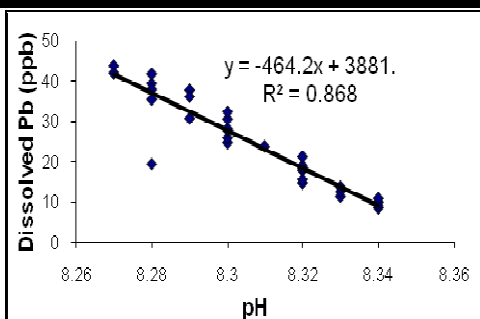


Fig.10. Inter-relationship between dissolved Pb and pH

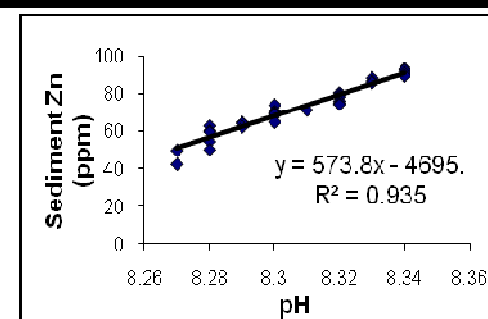


Fig. 11. Inter-relationship between sediment Zn and pH

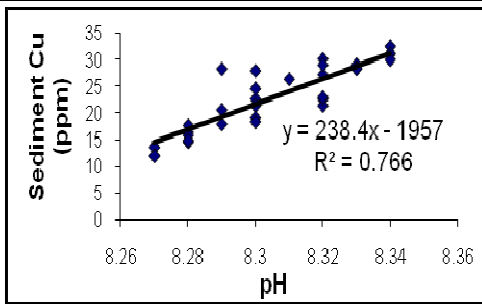


Fig.12. Inter-relationship between sediment Cu and pH

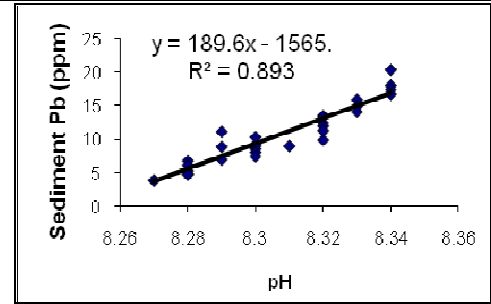


Fig.9. Inter-relationship between sediment Pb and pH