

Status of Heavy Metal in the Lower Gangetic Delta: Implication of Acidification on Compartmentation

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Abstract

Increased atmospheric carbon dioxide concentrations are causing greater dissolution of carbon dioxide into the estuarine water, which is the key factor behind today's ongoing ocean acidification and subsequent compartmentation of heavy metals in the system. We conducted a long term survey on temporal variation of pH and its impact on heavy metals in the Matla estuary, situated in the central part of Indian Sundarbans. The present study indicates the key role of acidification (major driver) in the exchange of heavy metals from sediment compartment to the overlying aquatic phase. The lowering of pH favours the process of dissolution of selected heavy metals (Zn, Cu and Pb) and promotes the transference of metallic compounds from the sediment to the aquatic phase.

Keywords: Acidification; Surface water pH; Dissolved heavy metals; Biologically available heavy metals in the sediment

Introduction

Over the last century, the atmospheric concentration of carbon dioxide has risen at a rate 100 times faster than any change observed during the past 650,000 years [1]. There is broad consensus that this ongoing change is a direct result of human activity, principally by fossil fuel burning, cement production and changing land use [2]. Atmospheric levels of carbon dioxide have consequently increased from pre-industrial levels of 280 ppm to a concentration of approximately 380 ppm [3]. Almost 50% of all anthropogenic carbon dioxide emitted to the atmosphere has diffused passively into the ocean, thereby significantly decreasing the rate of global warming [4]. Concentrations of atmospheric carbon dioxide are rising at a rate of 3.3% per year and will continue this rising trend [5]. Hydrological models predict that, based on proposed future emissions of carbon dioxide, the average oceanic pH will decline by 0.3–0.5 by the year 2100 and by 0.7 within the next 300 years [6]. Leakage from carbon dioxide seabed storage would create locally faster and stronger acidification than that induced by atmospheric carbon dioxide [7].

On the basis of the global trend of acidification, we try to focus on the issue at the local level in the Matla River situated in the central Indian Sundarbans of the lower Gangetic delta region and evaluate the role of the phenomenon on the compartmentation of selected heavy metals (Zn, Cu and Pb), that are dominant in the present geographical locale [8,9].

Materials and Methods

Study area

The lower Gangetic delta region, at the apex of Bay of Bengal sustains the famous mangrove dominated ecosystem, the Sundarbans. The central part of the delta complex receives the water of the Matla River. Industries are almost absent along the bank of the river, but the water is contaminated with sewage from the highly urbanized city of Kolkata. Reports of considerable concentrations of Zn, Cu and Pb are also available in this region, which originates mainly from the antifouling paints used for conditioning the fishing vessels and trawlers [8-12]. The present study was conducted 1.5 km off Bonnie camp (21°49'42.9"N/ 88°37'13.7"E) in the Ajmalmari river (local name) that receives the water from the Matla River.

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 from the sampling station using 10⁻¹ 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 HNO₃ as per the procedure of Danielsson et al. [13]. 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).

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

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

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 [14]. 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).

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

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

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

Surface water pH

The surface water pH exhibited variation within a small range. Highest value was recorded during 1985 (8.32) and lowest value (8.29) was recorded during 2013 (Figure 1). The gradual lowering of pH (0.001/yr) clearly confirms the phenomenon of acidification in the Matla estuarine system.

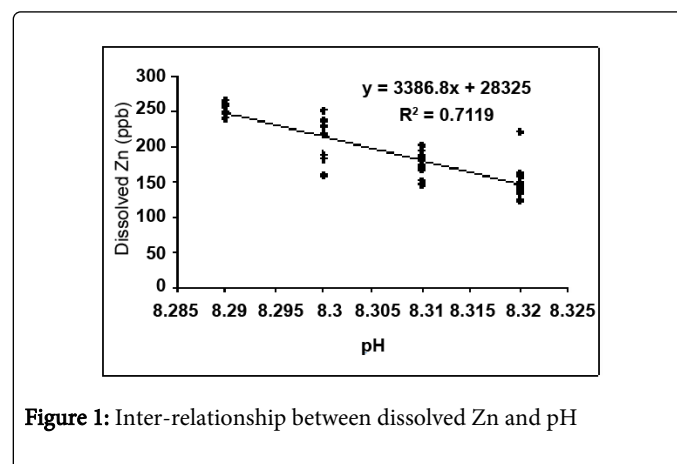


Figure 1: Inter-relationship between dissolved Zn and pH

Dissolved metal

The order of dissolved heavy metals in the estuarine water is Zn>Cu>Pb. Dissolved Zn ranged from 123.66 ppb during (1984) to 265.00 ppb during (2013) (Figure 2). Dissolved Cu ranged from 44.75 ppb during (1984) to 97.14 ppb during (2013) (Figure 3). During the study period the value of dissolved Pb ranged from 7.39 ppb (1984) to 17.39 ppb (2013). All the selected dissolved metals thus exhibit an increasing trend.

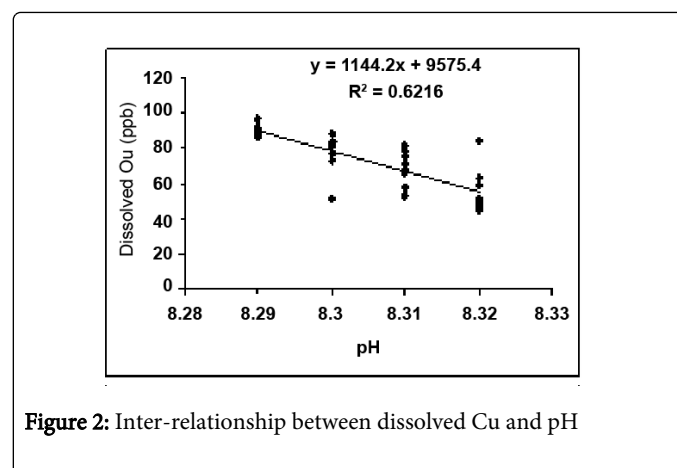


Figure 2: Inter-relationship between dissolved Cu and pH

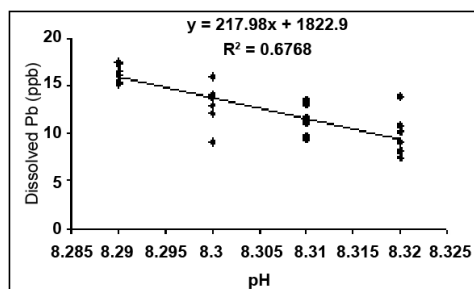


Figure 3: Inter-relationship between dissolved Pb and pH

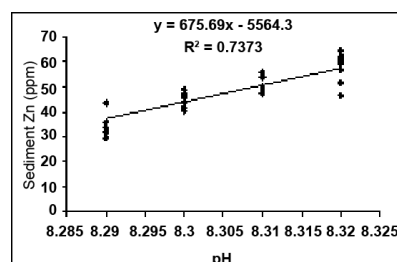


Figure 4: Inter-relationship between sediment Zn and pH

Sediment metal

In sediment compartment, the biologically available metals exhibited a decreasing trend. In case of Zn, the value decreased from 64.71 ppm (during 1984) to 29.66 ppm (during 2013). In case of Cu, the value ranged from 7.31 ppm (during 2013) to 23.61 ppm (during 1984). In case of Pb, the lowest value was observed during 2013 (1.08 ppm) and the highest value was recorded during 1984 (10.78 ppm). It is also noted that the order of biologically available heavy metals in sediment is similar to that of dissolved heavy metals (Zn>Cu>Pb).

Discussion

Ocean acidification is predicted to occur under current IPCC CO₂ emissions scenarios [15]. Around 50% of the emissions of carbon dioxide are being absorbed by the oceans, increasing the pCO₂ with a concomitant decrease in the surface pH by 0.3–0.4 units by the end of the century [3,16,17]. At present, the carbon dioxide interaction with seawater reduces the carbonate ion concentration, which is thought to regulate the calcification of extracellularly calcifying organisms [18,19]. This process is governed by the CaCO₃ saturation state (Ω (CO₃²⁻) (Ca²⁺)/K**sp*), where K**sp* is the apparent stoichiometric solubility product. For values of Ω <1 (undersaturated), seawater is corrosive, and dissolution may proceed [20]. The process triggers the rate of dissolution of precipitated heavy metals from the sediment compartment to the water column and alters the speciation of selected heavy metals in the study area. The scatter plots (Figures 1-6) explain the significant negative and positive relationships of aquatic pH with dissolved and biologically available heavy metals in surface sediments respectively.

The results suggest that heavy metal concentrations in coastal and estuarine waters need to be monitored considering the phenomenon of acidification, which is a major driver in altering the species of heavy metals in the coastal and estuarine ecosystem.

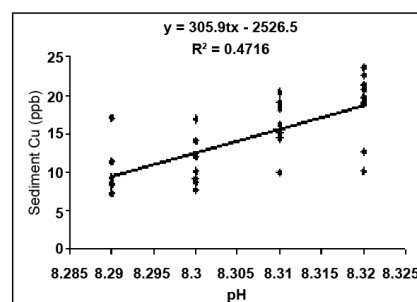


Figure 5: Inter-relationship between sediment Cu and pH

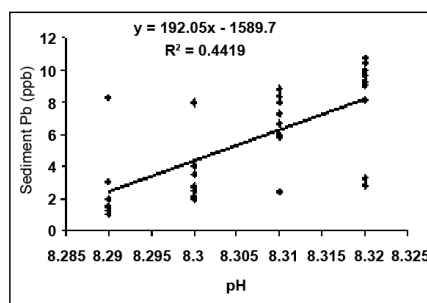


Figure 6: Inter-relationship between sediment Pb and pH

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