



Impact of acidification on heavy metal levels in a bheri of East Kolkata Wetlands (EKW), a Ramsar Site in the Indian sub-continent

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Abstract

EKW is situated at the eastern outskirts of the mega city of Kolkata, India (22°25' to 22°40' N and 88°20' to 88°35' E). It is a declared Ramsar Site and is of immense ecological importance. The fish ponds locally known as bheries of the area offers important ecosystem services such as microclimate maintenance, temperature regulation, flood control, recycling of municipal wastes and effluents (generated from urban and semi urban areas), fish production, livelihood, addition of aesthetic beauty etc. EKW is an extremely dynamic as well as ecologically sensitive ecosystem from the point of view of primary production and is a unique reservoir of a galaxy of phytoplankton, which serve as the foundation stone of food chain existing in the system. The economic wheel in an around the EKW is basically driven by the municipal as well as industrial waste materials that lead the secondary production (fisheries) by triggering the phytoplankton growth (primary producers). The waste materials from the highly urbanized and industrialized city of Kolkata, however, contain heavy metals such as Zinc, Copper, Manganese, Iron, Cobalt, Nickel, Lead, Chromium etc. that oscillate as a function of monsoonal run-off, environmental parameters etc. Among the environmental variables, pH has the major influence on the speciation of heavy metals. In this paper, an attempt has been made to assess the influence of aquatic pH on two major heavy metals namely Zn and Cu in the wetland ecosystem. A temporal analysis with more than three decades of pH data, dissolved as well as biologically available Cu and Zn in surface sediment/pond soil has been critically analysed. It is observed from the temporal trend of pH that the values have decreased over a period of more than three decades. It is also observed that dissolved Zn and Cu gradually increased over a period of time whereas biologically available Zn and Cu in the sediment have decreased simultaneously. This phenomenon confirms the regulatory role of pH in the process of speciation as a result of which precipitated metallic species of the underlying sediments undergo dissolution resulting in high values of dissolved heavy metals under a low pH situation. The present study is of immense importance as the process of acidification (gradual lowering of aquatic pH) accelerates the dissolved heavy metals in the aquatic phase due to which the floating food chain species such as plankton, carp variety of fishes might be affected through the process of bioaccumulation. Stabilizing the aquatic pH through application of measured doses of lime may be a roadmap to restore the situation.

Keywords: Eastern Kolkata Wetlands (EKW), acidification, heavy metal, bioaccumulation, roadmap

Introduction

East Kolkata Wetland (EKW) is a hotspot of biodiversity sustaining about 104 plant species, 40 avian species, 52 endemic fish varieties, 20 mammalian and various reptilian species. This vast area encompasses huge water bodies mainly bheries, which recycle the waste materials of the mega city of Kolkata into fish protein. The economic wheel in an around the EKW is basically driven by these waste materials that lead the secondary production (fisheries) by triggering the phytoplankton growth (primary producers). The waste materials from the highly urbanized and industrialized city of Kolkata, however, contain heavy metals like Zn, Cu, Mn, Fe, Co, Ni, Pb, Cr etc. that oscillate as a function of monsoonal runoff, environmental parameters etc. (Lakshmanan and Nambisan, 1983; Mitra, 2013). Among the environmental variables, pH has the major influence on the specification of heavy metals (Mitra et.al, 1992; Mitra et.al, 2010; Mitra, 2013; Mitra and Zaman, 2016). In this paper, an attempt has been made to assess the influence of aquatic pH on two major heavy metals namely Zn and Cu in the wetland system. It has been documented by several researchers that aquatic pH controls the process of dissolution/ precipitation and thereby regulates the level of heavy metals in the aquatic phase and the underlying sediment compartments (Ramamoorthy, 1988; Lakshmanan and Nambisan, 1983; Mitra et.al, 2011; Mitra et.al, 2012; Chakraborty et. al, 2009). On this background the present paper attempts to seek the reality of climate change by considering acidification as key player to regulate the fate of heavy metals in EKW bheries.

Materials and Methods

Study Area

EKW is situated at the eastern outskirts of the mega city of Kolkata, India (22°25' to 22°40' N and 88°20' to 88°35' E). The fish ponds of the area offers important

ecosystem services like flood control, recycling of municipal wastes and effluents (generated from urban and semi urban areas), aesthetic beauty, fish production, livelihood, etc. EKW is an extremely dynamic ecosystem from the point of view of primary production. It is an unique reservoir of a galaxy of phytoplankton, which serve as the foundation stone of food chain existing in the system. The present sampling site was selected at Natur Bheri (22°32'49.9" N to 88°25'30.1" E) with the aim to analyze the impact of acidification on the major heavy metals in the bheri.

Measurement of aquatic pH

The pH of the surface water in the selected bheri was measured with a portable pH meter (sensitivity = ± 0.02).

Analysis of dissolved Zn and Cu

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 HNO₃ as per the procedure of Danielsson et al (1978). Extracts were analyzed for Zn and Cu 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 \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

Analysis of biologically available Zn and Cu from bheri soil samples

Soil samples from 1 cm depth below the surface were collected by scrapping 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). The resulting solutions were then stored in polythene containers for analysis. The solutions were finally aspirated in the flame Atomic Absorption Spectrophotometer (AAS) (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 (μgg^{-1})	Laboratory results (μgg^{-1})
Zn	28.6	26.2
Cu	14.9	13.7

Statistical Analysis

Inter-relationships between aquatic pH, selected dissolved heavy metals and biologically available heavy metals in aqueous sediment were determined through correlation coefficient values. 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 1986 (8.07) and the lowest value (7.81) was recorded during 2015 (**Fig. 1**). The gradual lowering of pH ($8 \times 10^{-3}/\text{yr}$) clearly confirms the phenomenon of acidification of estuarine water in the study area.

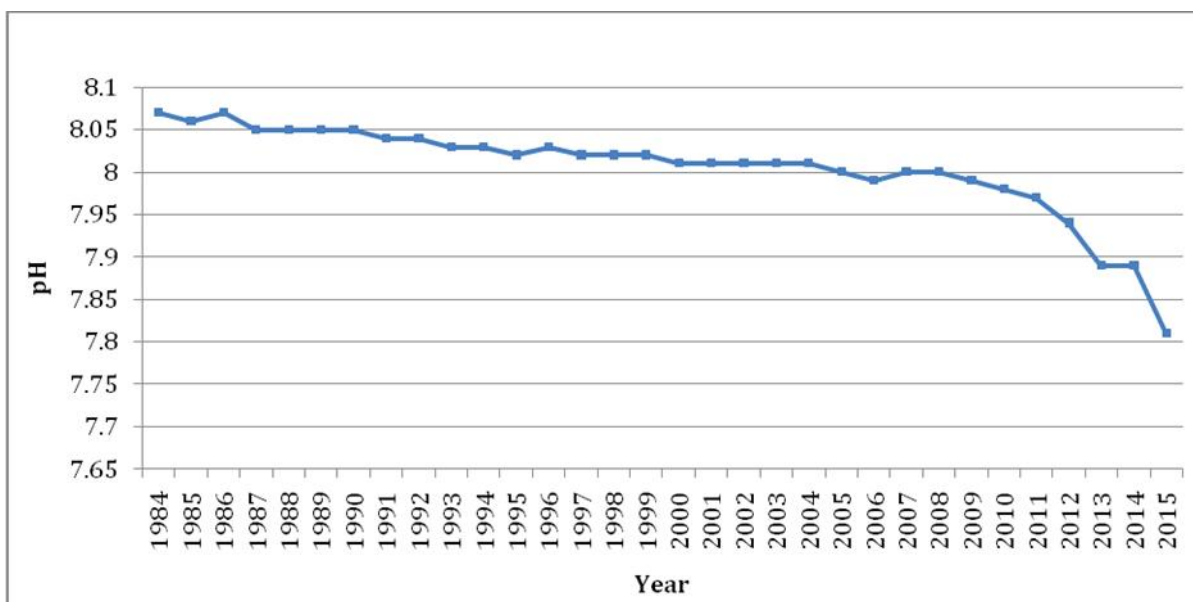


Fig 1: Temporal trend of pH over a span of more than three decades

2. Dissolved metal

The order of dissolved heavy metals in the estuarine water is Zn > Cu. Dissolved Zn ranged from 472.8 ppb

during (1984) to 918.48 ppb during (2015) (Fig. 2). Dissolved Cu ranged from 130.62 ppb during (1984) to 389.75 ppb during (2015) (Fig. 3).

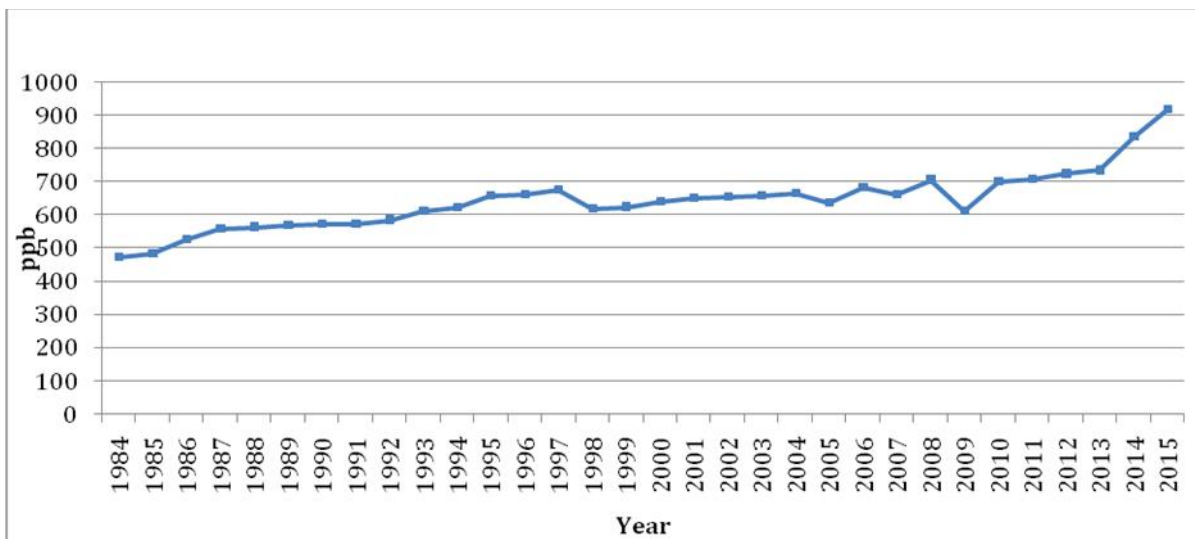


Fig 2: Temporal trend of dissolved Zn in EKW over a span of three decades

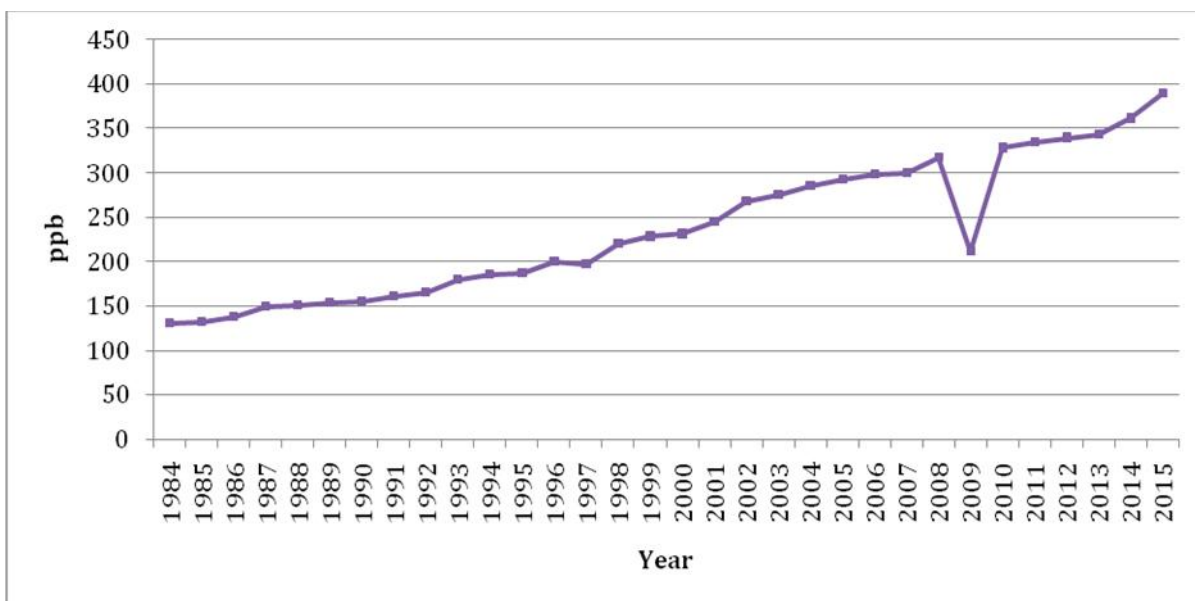


Fig 3: Temporal trend of dissolved Cu in EKW over a span of three decades

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 135.19 ppm (during 1984) to 74.1 ppm (during 2015) (Fig. 4).

In case of Cu the value ranged from 78.74 ppm (during 1984) to 49.55 ppm (during 2015) (Fig. 5). It is also noted that the order of biologically available heavy metals in sediment is similar to that of dissolved heavy metals (Zn > Cu).

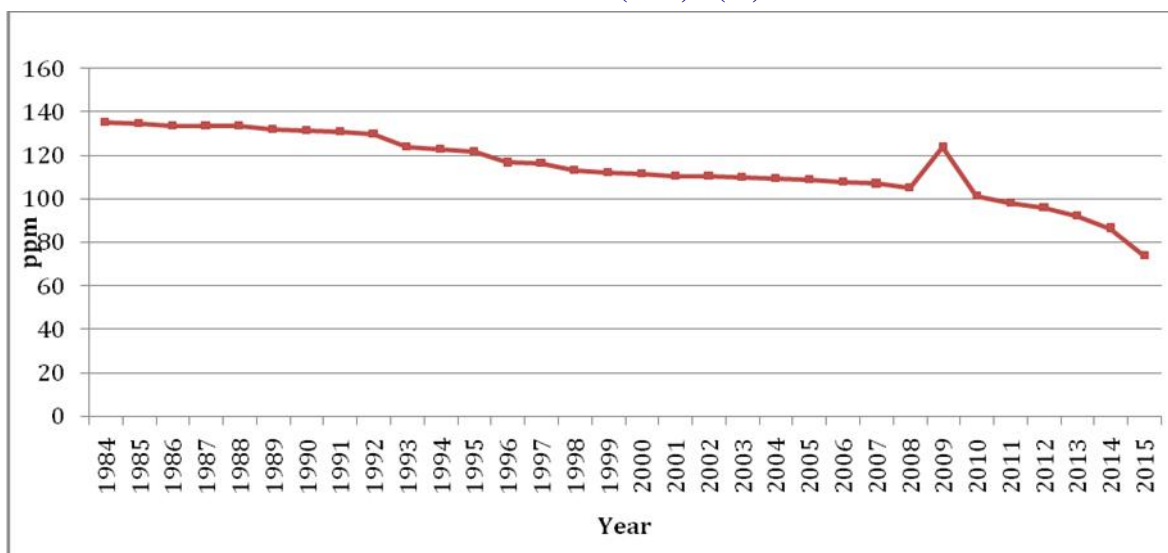


Fig 4: Temporal variation of Biologically Available Zinc (BAZn) in sediment/soil compartment of Natur bheri

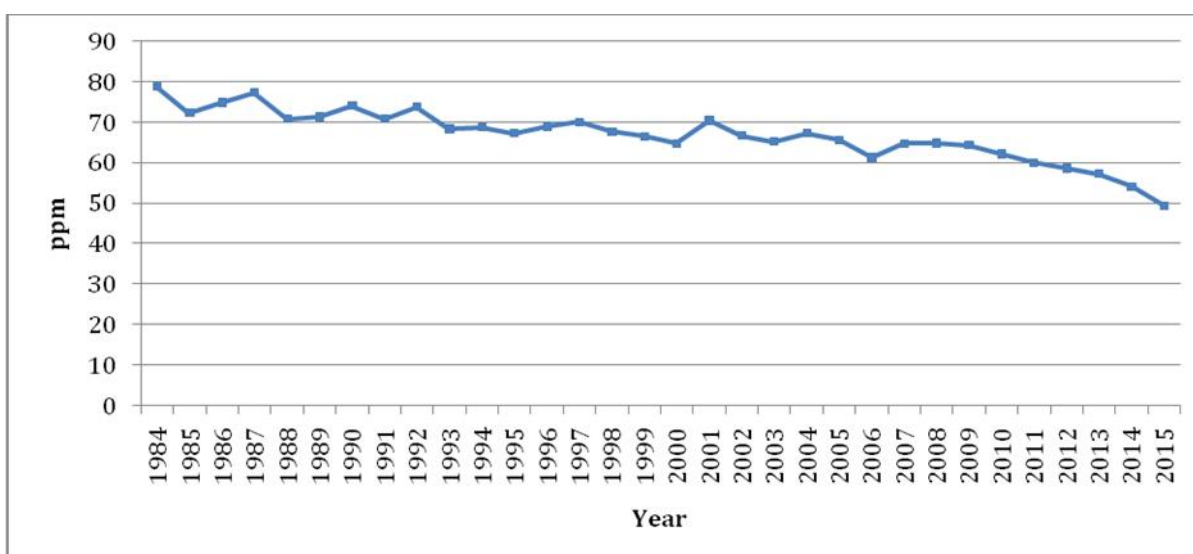


Fig 5: Temporal variation of Biologically Available Copper (BACu) in sediment/soil compartment of Natur Beheri

Discussion

The major sources of heavy metals in the EKW are the industrial and municipal wastes from the metropolitan city of Kolkata. The city wastes are of complex nature consisting of mixture of organic wastes, heavy metals, pesticides, oil and grease. Adjacent to the EKW, the Bidyadhari-Matla channel is located where large number of fishing vessels and trawlers operate throughout the day. The antifouling paints used for conditioning these fishing boats and trawlers contribute appreciable amount of Zn and Cu in the adjacent water bodies which enter our study area during high tide phase. It is observed from the temporal trend of pH that the values have decreased

over a period of more than three decades. This may be attributed to gradual increase of carbon dioxide in the atmosphere, which dissolves in the aquatic phase to form carbonic acid, thus pushing the equilibrium towards acidic value. It is also observed that dissolved Zn and Cu gradually increased over a period of time whereas biologically available Zn and Cu in the sediment have decreased simultaneously. This phenomenon confirms the regulatory role of pH in the process of speciation as a result of which precipitated metallic species of the underlying sediment/surface soil of the bheri undergo dissolution resulting in high values of dissolved heavy metals under a low pH situation (Table 2).

Table 2- Correlation analysis of selected parameters in Natur Bheri

Combination	r- value	p- value
pH × BA _{Zn}	0.9182	<0.01
pH × Dissolved Zn	-0.9223	<0.01
pH × BA _{Cu}	0.9345	<0.01
pH × Dissolved Cu	-0.8598	<0.01

BA_{Zn} = Biologically available Zn from bheri surface soil; **BA_{Cu}** = Biologically available Zn from bheri surface soil.

The above correlation values act as litmus test to the framework of climate change impact on metallic species. The highly significant negative correlation between the pH and dissolved Zn and Cu ($r_{\text{pH}} \times$ dissolved Zn = -0.9223, $p < 0.01$; $r_{\text{pH}} \times$ dissolved Cu = -0.8598, $p < 0.01$) and highly significant positive correlations between pH and BA_{Zn} and BA_{Cu} in the surface sediments as analyzed from the data ($r_{\text{pH}} \times$ BA_{Zn} = 0.9182, $p < 0.01$; $r_{\text{pH}} \times$ BA_{Cu} = 0.9345, $p < 0.01$) confirms pH as the pivotal player that runs the wheel of compartmentation of heavy metals in the EKW bheries. The present study is of immense importance as the process of acidification (gradual lowering of aquatic pH) accelerates the dissolved heavy metals in the aquatic phase through which the floating food chain species such as plankton, carp variety of fishes might be affected through the process of bioaccumulation. Stabilizing the aquatic pH through application of measured doses of lime may be a roadmap to restore the situation.

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