Influence of Aquatic pH on Dissolved Pb in East Kolkata Wetlands: A Case Study With Reference to Climate Change Induced Acidification

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Research Article

Keywords: Eastern Kolkata Wetlands (EKW), acidification, Lead, pH, Carbon-dioxide

Posted Date: June 9th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-577162/v1

Abstract

The present study was undertaken with the databank of dissolved Pb and pH of the aquatic system in the East Kolkata Wetlands, an internationally unique Ramsar Site of Eastern India during a period of twenty years (2000-2019). Our study site is receiving huge amounts of domestic and industrial wastewater from surrounding areas of highly populated metropolitan city of Kolkata. The data on pH exhibits a decreasing trend with the passage of time, which may be attributed to the phenomenon of acidification in which CO_2 dissolves with the water and shifts the pH to a lower value. This may result in the dissolution of accumulated Pb in the sediment and transfer the same to the overlying aquatic phase. The increasing trend of dissolved Pb confirms the hypothesis. The significant negative correlation between pH and dissolved Pb ($r= -0.7763$; $p\leq0.01$) supports the view of the regulatory effect of pH on the dissolved Pb level in the aquatic systems of East Kolkata Wetland.

1. Introduction

Freshwater ecosystems are globally declining at an astronomical rate (MEA, 2005; Dudgeon *et al*. 2006). This holistic degradation of wetlands is triggered by unprecedented changes instigated by global climate crisis. A bouquet of factors is responsible for this phenomenon which includes anthropogenic driven landscape changes, species loss, biodiversity deterioration etc. (Allan and Flecker, 1993; Lemly, *et al*., 2000; Kingsford, *et al*., 2006). Wetland loss finds prominence with degradation of Aral Sea (Micklin, 1988) and Marshlands of Mesopotamia (Partow, 2001). Global temperature rise has not only resulted in wetland shrinkage in the arid zones of the world but also impacted the water volumes of downstream wetlands and estuaries (Kingsford *et al*. 2006). Scarcity in rain-fed river water volume and species loss is a testimony to the fact. Pollution load and acidification has caused irreversible damage on wetland ecology; the flora and fauna in particular. Examples include small lakes in northern Ontario (McNiol, *et al*., 1987) aquatic resources across North America, eastern Canada and Scandinivia (Baker, 1991), coastal wetlands of eastern Australia (White, *et al*., 1997). Nitrogen deposition and eutrophication of freshwater systems of Asia is a matter of grave concern and may be more important than Sulphur deposition. Regional acidification of soil is notable in parts of Eastern Asia (Duan, *et al*., 2016). Incidences of Nitrogen and Sulphur accumulation is observed in parts of India, Bangladesh, Pakistan, Myanmar, Thailand, Laos, North Korea, and Japan (Vet *et al*., 2014). Early acid deposition effects are recorded in Asia by (Bhatti, 1992). Global climate changes have direct and indirect impacts on patterns of biogeochemical cycling as well leading to decreasing pH trends in precipitation in southern China (Zhao and Sun, 1986; Galloway *et al*., 1987), south-eastern coastline and north-eastern India (Varma, 1989), in Japan (Hara, 1997) and Korea (Chung *et al*., 1996). Spatio-temporal assessments and ecosystem level surveys points to ecosystem degradation with increasing acid deposition effects. For example, acidification has led to mass elimination of freshwater fishes as recorded by (Hendrey, 1981).

The eastern peripheries of Kolkata, one of the most prominent cities in the eastern part of Indian subcontinent are bordered by East Kolkata Wetlands (EKW). It is one of the largest single-stretch aquaculture belts of the world with identified resource recovery opportunities thus increasing the total economic value of the wetland systems manifold. This wetland is currently under the double pronged impact of anthropogenic stress factors and climate fluctuations in the lower gangetic belts. The wastewater draining off perennially from in and around the city having recognizable limits of trace and toxic heavy metals such as Zinc, Copper, Manganese, Iron, Cobalt, Nickel, Lead, Chromium, Mercury reaches to EKW leading to subsequent dissolution and precipitation in the ambient media (Lakshmanan and Nambisan, 1983; Mitra, 2013). pH is one of the primary determining factors on heavy metal specification among other environmental variables (Mitra et.al, 1992; Mitra et.al, 2010; Mitra, 2013; Mitra and Zaman, 2016; Dutta *et al.*, 2016). Slight changes in pH might cause humongous effects on wetland flora and fauna leading to major ecosystem losses worldwide. The cascading effects of global climate changes and anthropogenic stress is an adage to the problem. Several authors have been documenting how the regulatory role of pH on patterns of heavy metal accumulation but not much light is thrown on the issue of holistic restoration of ecosystems ameliorating the crisis (Ramamoorthy, 1988; Lakshmanan and Nambisan, 1983; Mitra et.al, 2011; Mitra et.al, 2012; Chakraborty et. al, 2009). The current study attempts to investigate in that direction the influence of aquatic pH on dissolved Lead in EKW with reference to acidification in freshwater systems induced by global climate change; a burning issue of our times. The bioaccumulation pathway of toxic heavy levels in the different trophic levels of the ecosystem is discussed in (**Fig. 1**).

2. Material And Methods

2.1 Study Area

EKW is strategically located ($22^{0}25'$ to $22^{0}40'$ N and $88^{0}20'$ to $88^{0}35'$ E) very important group of wetlands designated as ‘Kidneys of Kolkata’. The fish ponds of the area locally termed as ‘bheries’ are unique in their value based services such as regulation of urban flood water, high-tide water influx, recycling of the sewage and effluents (generated from urban and semi urban areas), and a basket of livelihood options which include the concept of ‘resource recovery’. Sampling site was selected at *Natur Bheri* ($22^{0}32'49.9''$ N to $88^{0}25'30.1''$ E), one of the large and centrally located ponds in EKW. The layout map (**Fig. 2**) and study area base map is studied (**Fig. 3**) while the study area classified map is illustrated in (**Fig. 4**).

2.2 Measurement of aquatic pH

Potable pH meter (sensitivity = ±0.02) was used for aquatic pH measurements.

2.3 Analysis of dissolved Lead from water samples

A standard procedure of dissolved lead analysis from water samples collected from the study area was done as per the protocol suggested by (Danielsson, *et al.*, 1978). Heavy metal analysis was done by

Atomic Absorption Spectrophotometer (AAS) (Perkin Elmer: Model 3030). The accuracy of the procedure was confirmed with respect to reference values **(Table 1)** using seawater materials (CASS 2).

Table 1: Analysis of lead in sea-water samples (CASS 2)

Element	Certified value (μgl^{-1})	Laboratory results (μgl^{-1})
Pb	0.019 ± 0.006	0.029 ± 0.009

2.4 Analysis of biologically available Pb from bheri soil samples:

Standard soil sampling procedures were followed and analysis was done as per the standard procedure outlined by Malo (1977). Heavy metal analysis was similarly carried by AAS. Reagent blank shows no trace of heavy metals.

2.5 Statistical Analysis

Relationship between aquatic pH and dissolved heavy metal in the aqueous sediment were determined by calculating the correlation coefficients. All statistical calculations were performed using the SPSS 9.0 software suite for Windows.

3. Results

3.1 Surface Water pH

The pH of the surface water demonstrated considerable fluctuations over the large time period of more than three decades with decreasing trends in the last few years (Fig. 5) as per our previous observations. The gradual decrease in pH (8×10^{-3}/yr) points to acidification of wetlands. In the current study, pH data until 2018 is observed (Fig. 8) which shows similar trends.

3.2 Heavy metal dissolution in aqueous medium:

The graphical representation of accumulation pattern of Lead is shown in (Fig. 6) and the temporal pattern of Lead dissolution is further shown in (Fig. 8). The annual variations of Lead dissolved in water shows an increasing concentration pattern across the years (2016-18). The accumulation is recorded to be the highest during the monsoon season, followed by the post-monsoon, winter and finally the pre-monsoon season. This is due to unlock of heavy metals from sediment compartments and dissolution in water with monsoonal run-off. Similar trends are observed by (He, *et al.*, 1997). This might be due to the following reasons as detailed under:

a)Prolonged monsoon and increased run-off from adjacent peri-urban landscapes in the lower gangetic belts.

b)Churning effect of the sediments which are the reservoir of heavy metals.

c)Lowering of pH due to freshwater influx in the wetland system leading to heavy metal dissolution from the sediment compartments to the overlying water columns.

3.3 Heavy Metal dissolution in sediment compartments

The pattern of Lead accumulation in the sediment compartments is revealed in (Fig. 7). The temporal variation of bioavailable metals in the sediment demonstrated a similar increasing trend between 2016 and 2018. However, the seasonal variations shows the pattern premonsoon > winter > postmonsoon > monsoon. This reverse seasonal accumulation trend is due to evaporation of water during the summer months and relatively high pH values in the aqueous columns leading to acidification. Moreover, decadal climate change is also encouraging the acidification in ambient media leading to increased heavy metal concentrations. The precipitation of heavy metals in sediment columns is significantly altering the soil ecology and bioaccumulation across different trophic levels of freshwater ecosystems.

3.4 Correlation between dissolved Pb and aquatic pH

The strong negative correlation between pH and dissolved Pb ($r = -0.7763$; $p \leq 0.01$) supports the view of the regulatory effect of pH on the dissolved Pb level in the aquatic systems the study area as described in (Table 2). The correlation values conclusively prove the regulatory role of aquatic pH on dissolve heavy metal in aqueous systems.

Table 2: Correlation table between Pb and pH

Correlation Table between Pb and pH

	Lead	pH
Lead	1	
pH	- 0.77663	1

4. Discussion

Unregulated urbanization patterns coupled with the lack of proper wastewater management facilities leads to an influx of sewage and polluted water into the East Kolkata Wetland system. A large number of fishing vessels and trawlers operate throughout the day in the Bidyadhari-Matla channel which is adjacent to the EKW. The Lead containing antifouling paints which are commonly used to condition these boats and trawlers leach into the adjacent water bodies. During the high tide, this lead enters our study area. Moreover, the East Kolkata Industrial Area and the various illegal factories in Chowbagha as well as the tanneries in the Kolkata Leather Complex at Karaidanga, Bantala contribute significantly to huge entry of toxic metals such as Lead, Cadmium, Chromium and Mercury in the system. The lack of proper source segregation of waste and an effective management system for solid waste contributes to the monstrosity of the problem. EKW works as ‘Kidneys of Kolkata’ and contributes in organic degradation of the sewage and wastewater leading to ‘resource recovery’ and ‘positive ecological feedback’. However, the toxic heavy metals remain locked in the sediment compartments and precipitate below the aqueous medium leading to their bioaccumulation in the fishes and vegetables harvested in and around EKW, thus making their way into the food plates of consumers. Analysis of the temporal trend of pH over the past three decades point to an overall reduction of pH. This may be attributed to the gradual increase of atmospheric carbon dioxide levels which promotes the dissolution of carbon dioxide in the aquatic phase. This results in the formation of carbonic acid which pushes the ionic equilibrium of the water body towards more acidic values. The Pb dissolved in both the aqueous and sedimental fractions of the EKW were also observed to have increased over time. Seasonal accumulation of Pb in water (**Fig. 6**) and sediments (**Fig. 7**) points to an inverse relationship the reasons being discussed before.

The global temperature and carbon-dioxide concentrations (which have been progressively increasing over the past century, primarily due to anthropogenic activities) and the environmental parameters share a directly proportional relationship. Global rise in temperature is leading to pH decrease in freshwater ecosystems across the world thus compromising the wetland biodiversity on a mass scale. A slight change in the pH might wreak havoc in the fragile freshwater ecosystems which are already under a bouquet of anthropogenic stress factors.

Increasing acidity in aqueous medium prompts the unlocking of heavy metals from sediment compartments facilitating in the process of dissolution in the aqueous medium leading to high heavy metal concentration in water. The strong negatively correlated relationship between the pH and dissolved Pb concentration confirms pH to be the key player that runs the wheel of compartmentation of heavy metals in the EKW bheries. The present study opens up a new vista where anthropogenic climate change is accelerating the process of acidification in global freshwater systems and increasing heavy metal toxicities in the ambient media. The gradual decrease of aquatic pH (acidification) is responsible for the release of dissolved heavy metals into the aquatic phase. Different species of plankton, carp variety of fishes might be affected through the process of bioaccumulation resulting in the infiltration of heavy metals into our food web. At attempt to stabilize the aquatic pH by the controlled addition of lime may be a potential approach to restore the integrity of the situation. This approach may also help us further establish ecological sustainability in the internationally unique group of wetlands.

5. Declaration

Funding

No immediate funding sources are involved.

Conflicts of interest/Competing interests

The authors declare that the current publication has no conflict of interest, whatsoever.

Availability of data and material

Not applicable

Code availability

Not applicable

Authors' contributions

Joystu Dutta has contributed in conceiving the current research and implementation of field level data collection as well as initial drafting of the manuscript. Joysurya Dutta has helped in the process of data collection and analysis. TS has helped in data validation and final manuscript editing. SZ has reviewed the manuscript. AM supervised the entire research work and the preparation of the manuscript.

Ethics approval

Not required

Consent to participate

Not applicable

Consent for publication

All the authors are mutually agreed to publish the manuscript.

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Figures

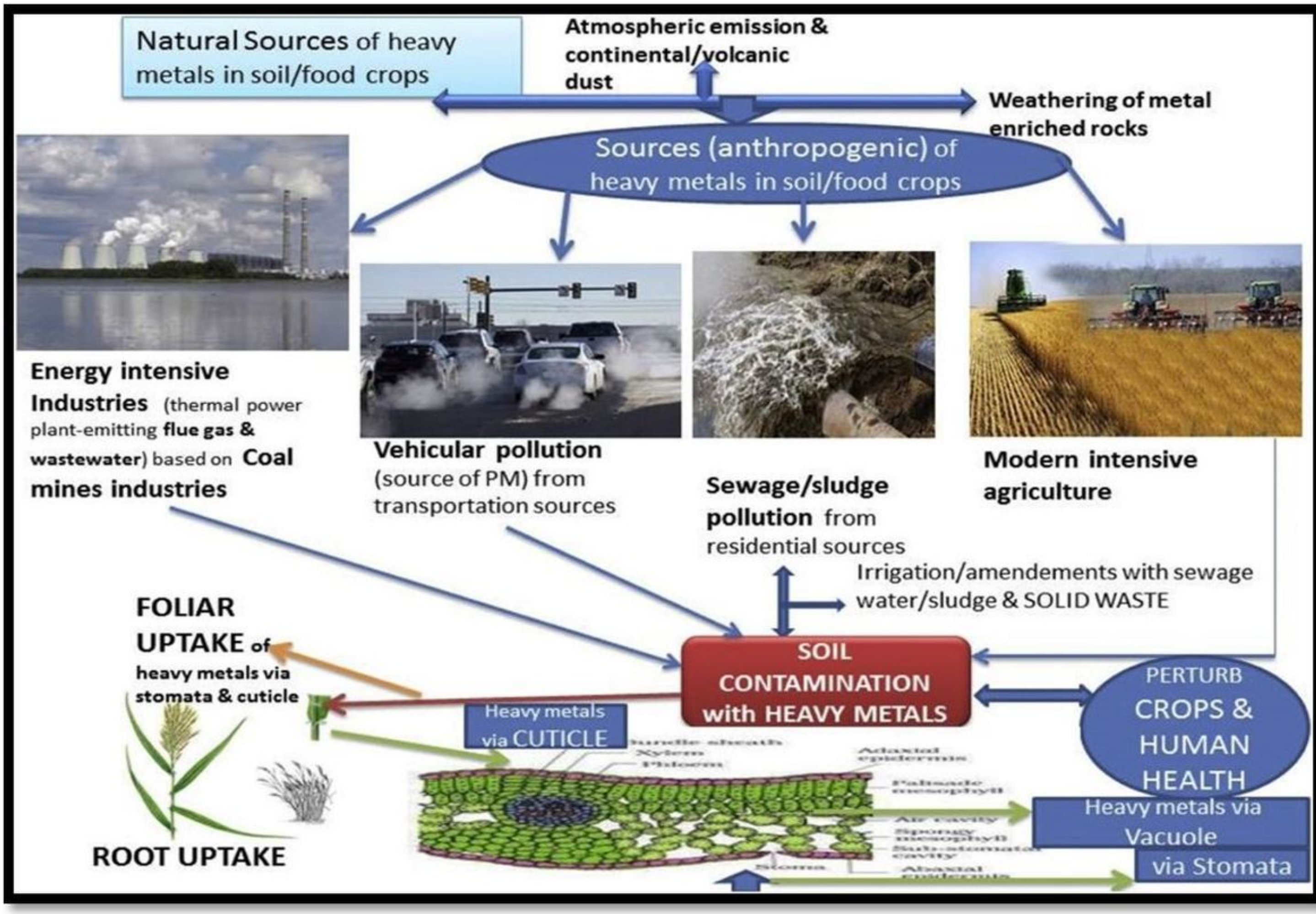

Figure 1

Illustration showing bioaccumulation of toxic heavy metals such as lead in the different trophic levels of the ecosystem.

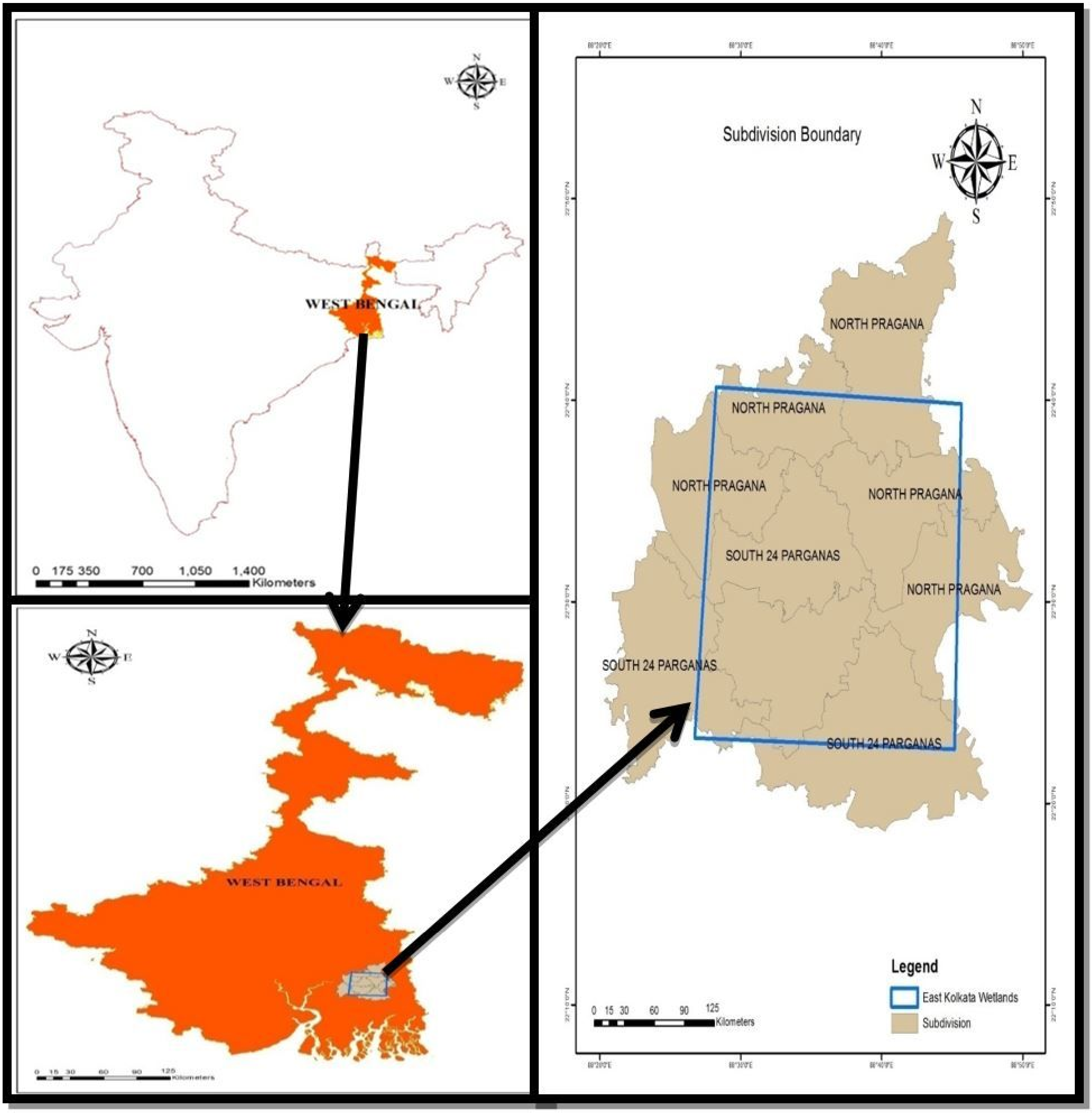

Figure 2

Layout map of the East Kolkata Wetlands. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

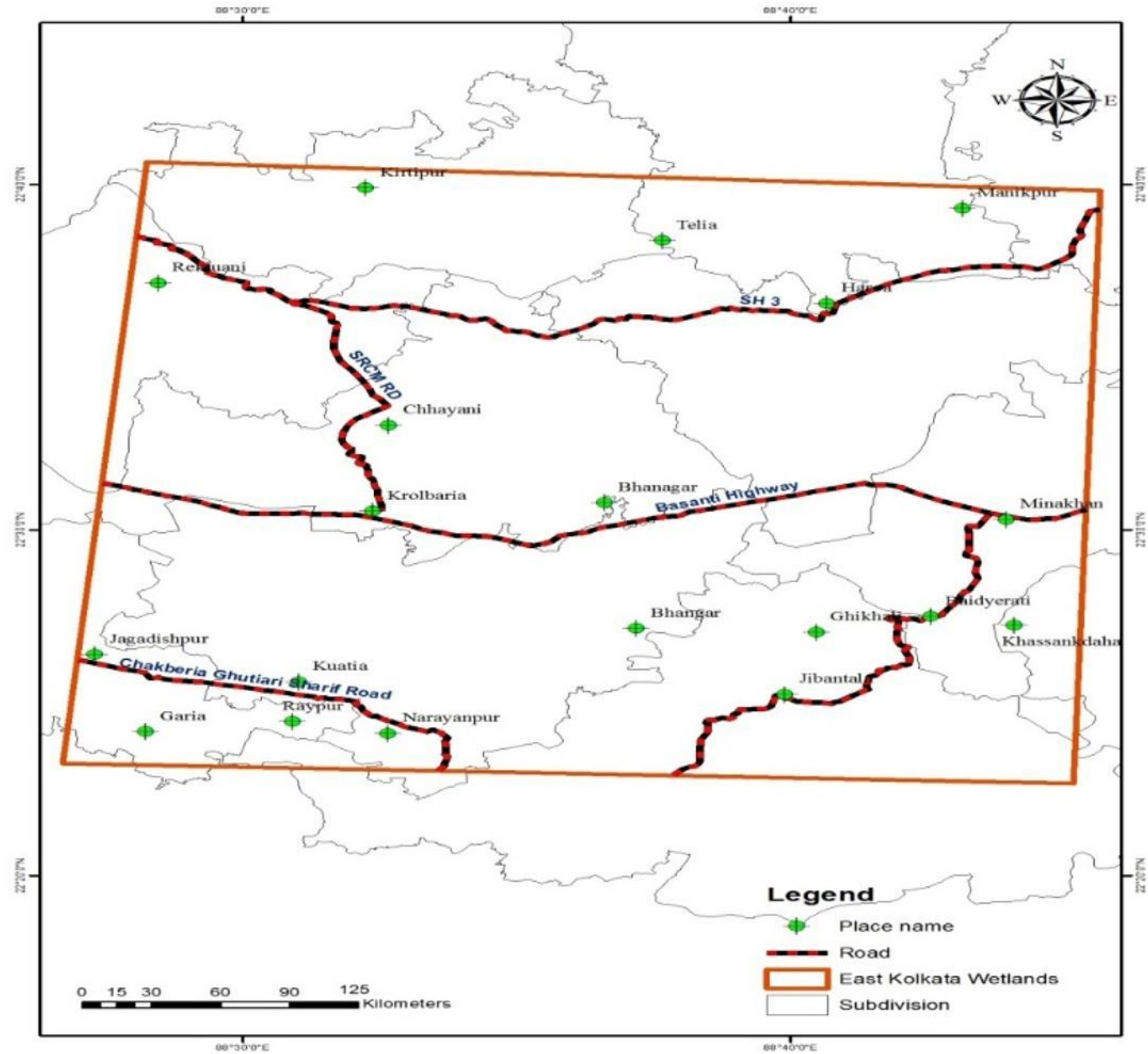

Figure 3

Base map of the study area. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

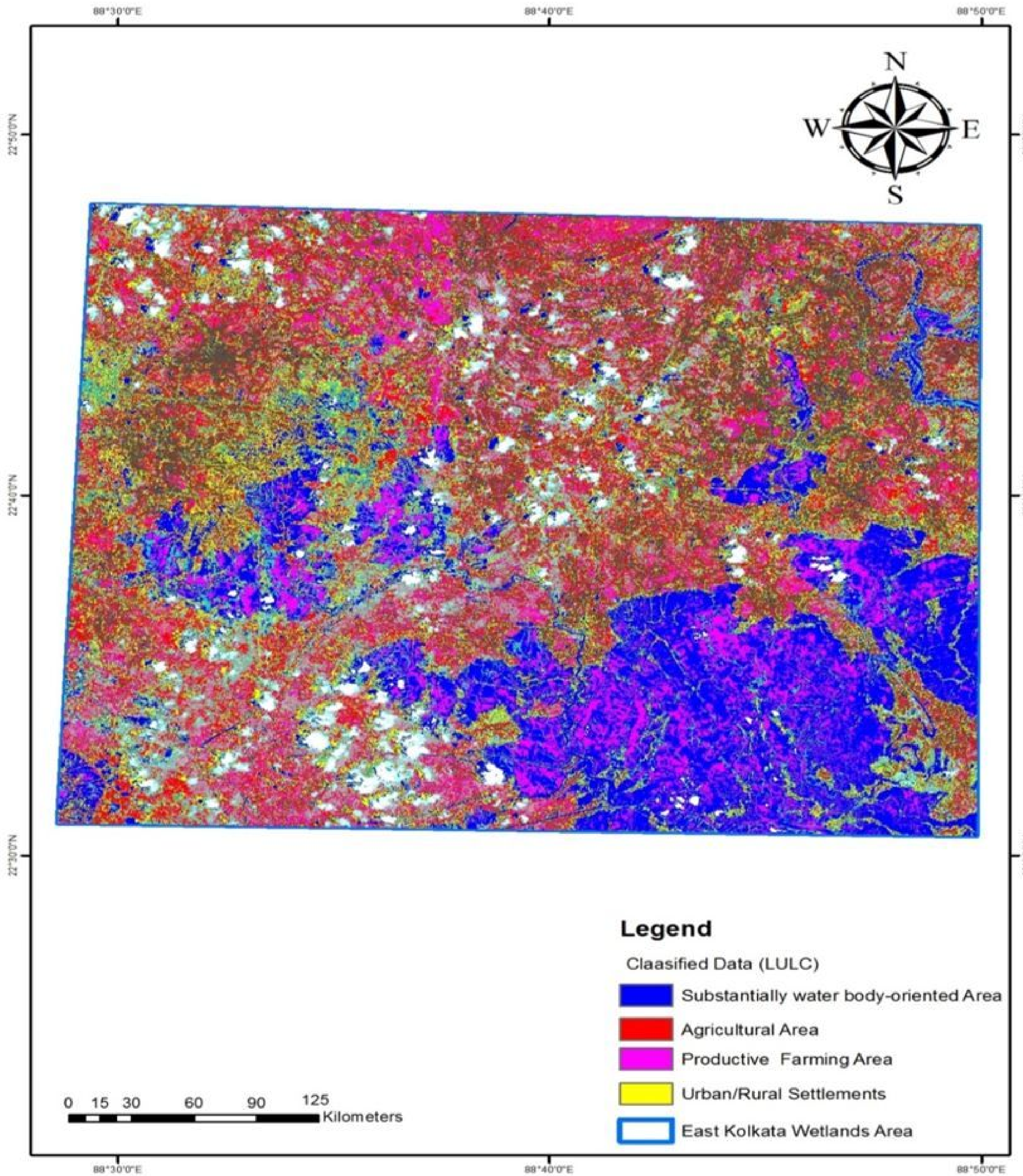

Figure 4

Classified map of the study area. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

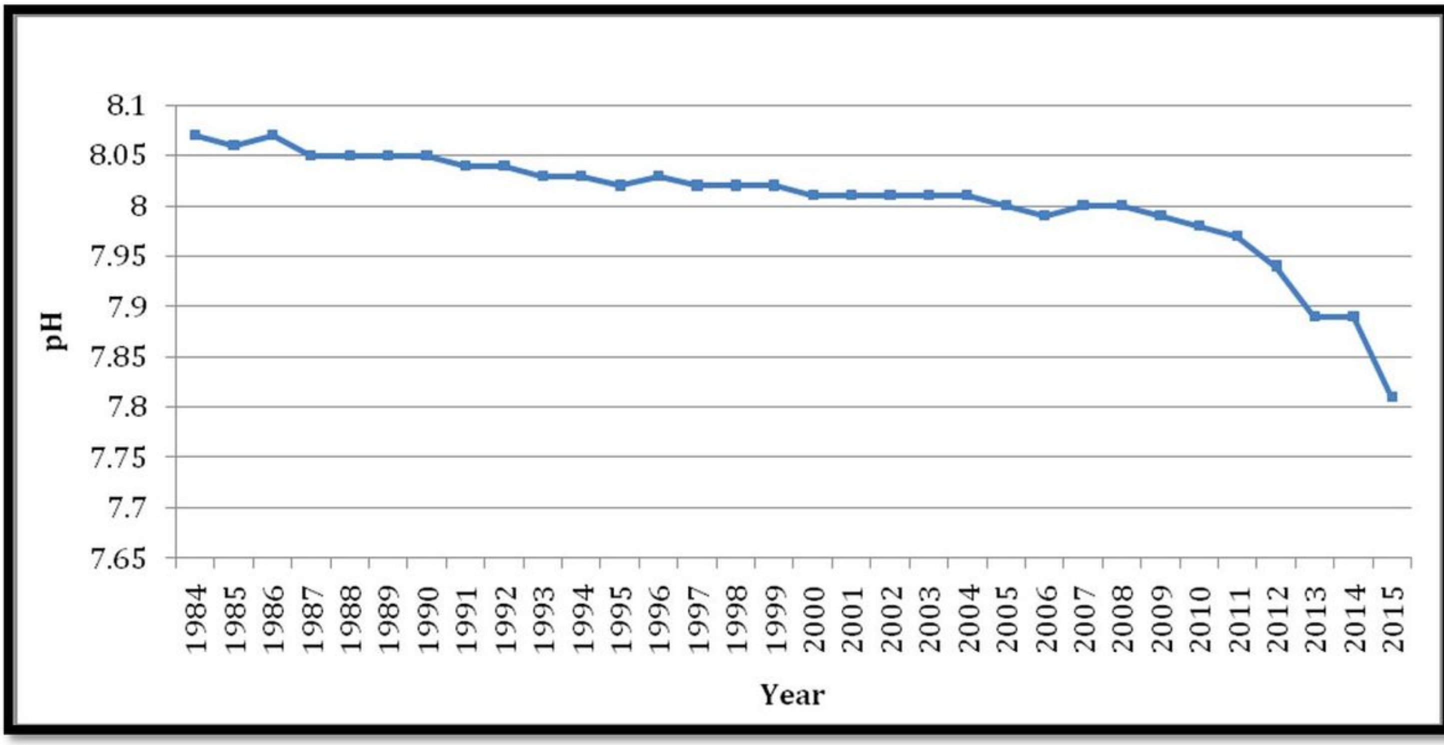

Figure 5

Historical trend of pH in the East Kolkata Wetlands

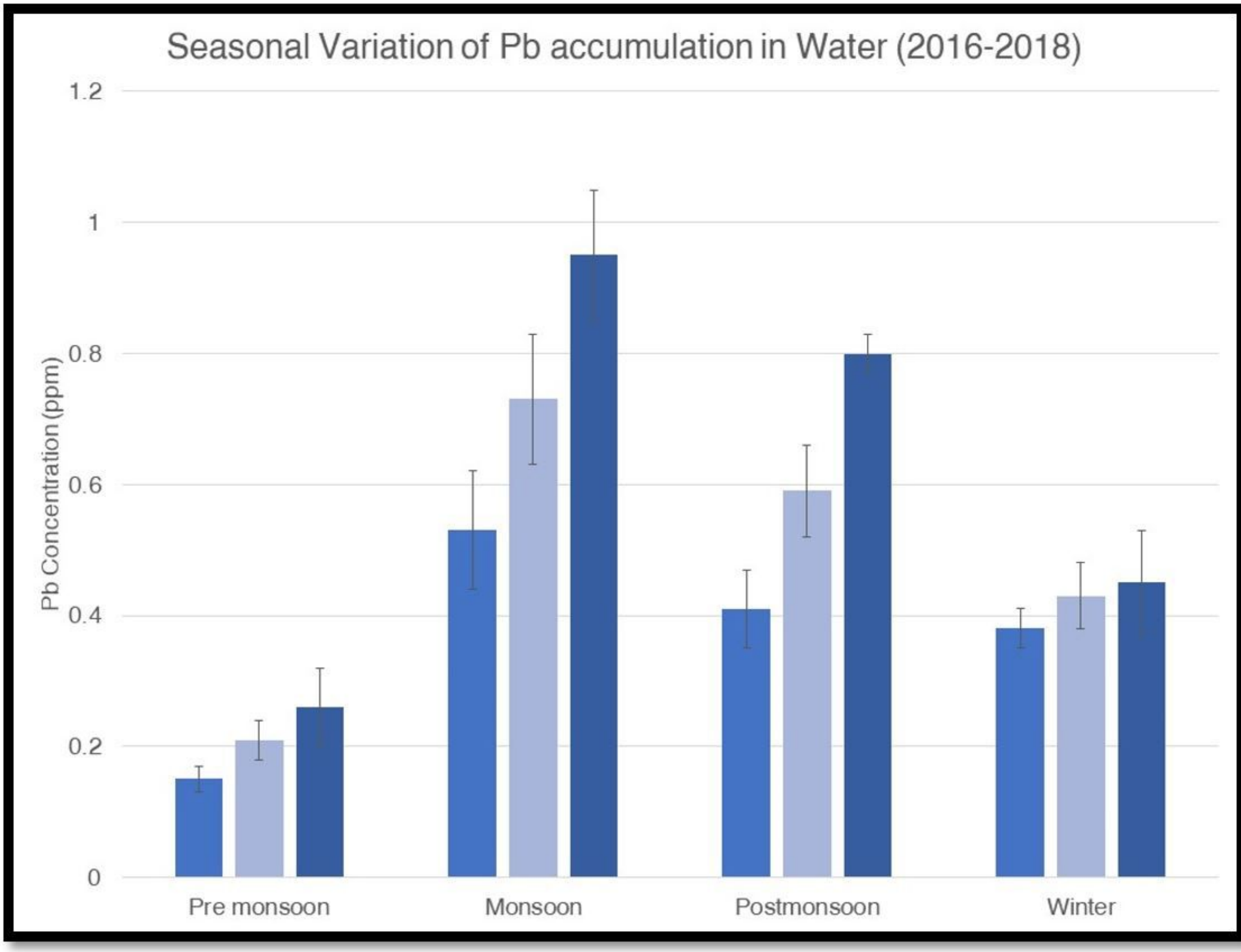

Figure 6

Seasonal variation of lead accumulation in water

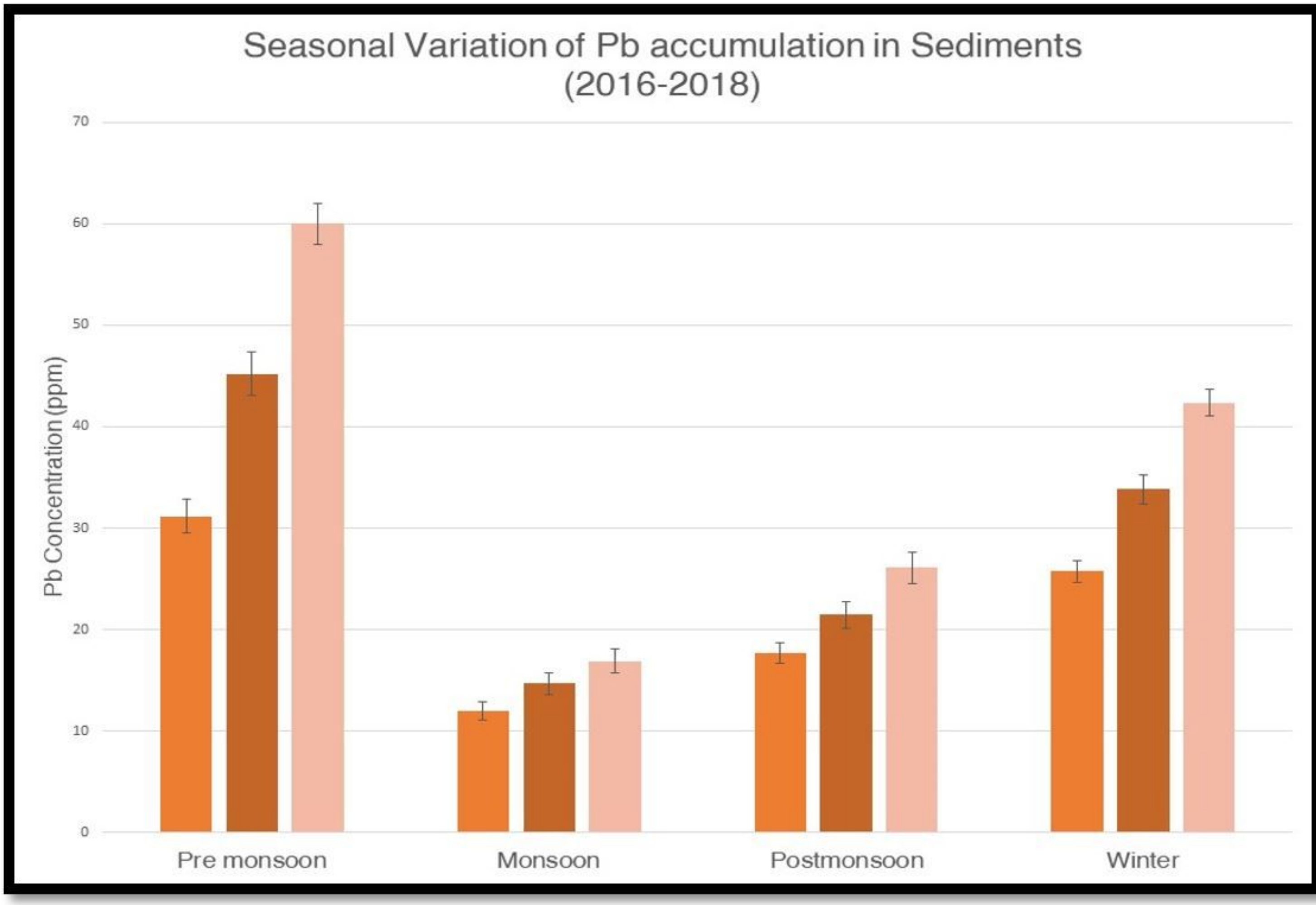

Figure 7

Seasonal variation of lead accumulation in sediments

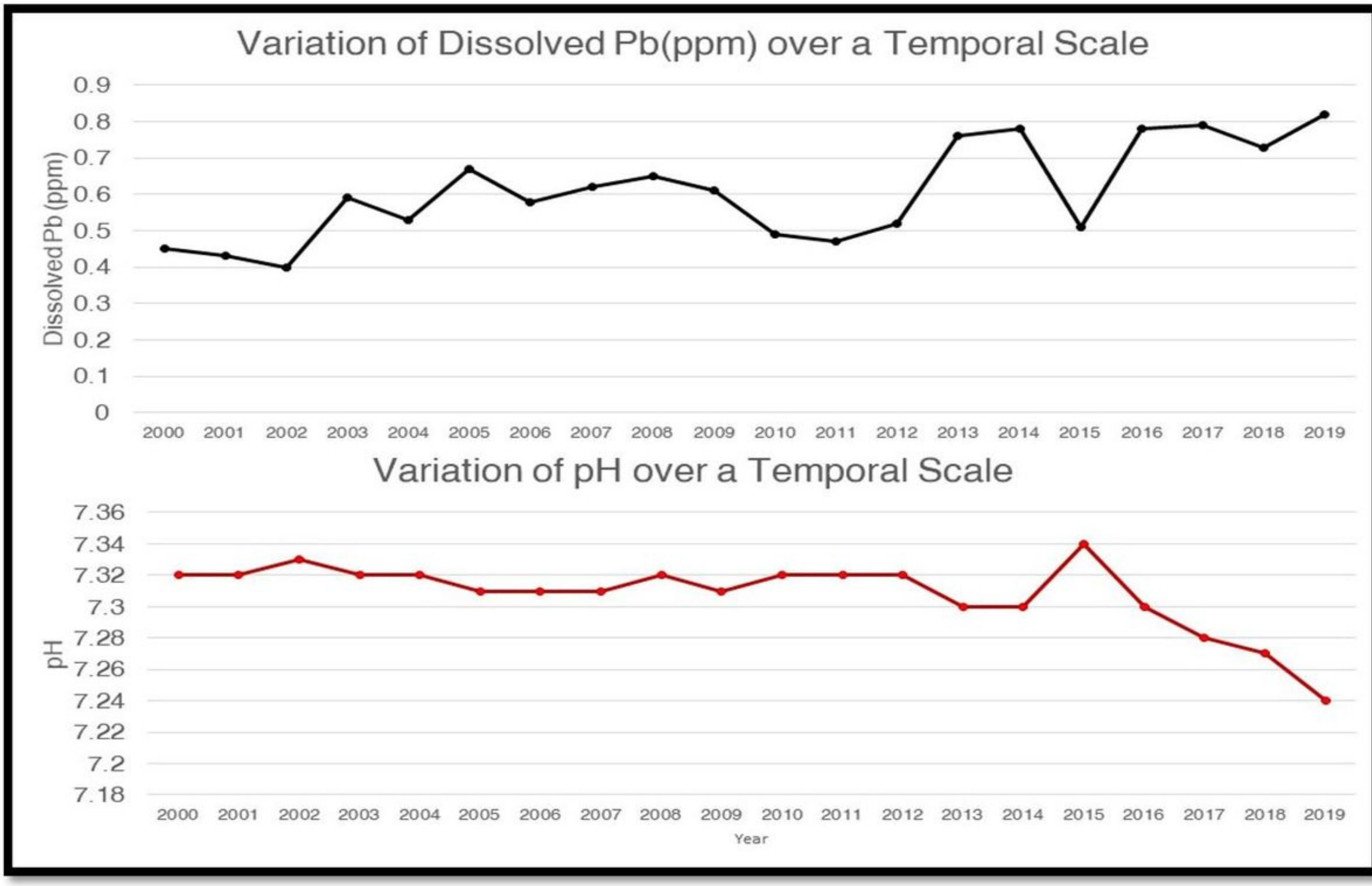

Figure 8

Comparative variation of dissolved lead (ppm) and pH over a period of two decades