Tracing Nitrogen and Carbon Biogeochemical Processes in the Inter-tidal Mangrove Ecosystem (Sundarban) of India and Bangladesh: Implications of the Global Environmental Change

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Project Reference Number: ARCP2012-07CMY-Ramanathan
Final Report submitted to APN

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OVERVIEW OF PROJECT WORK AND OUTCOMES

Non-technical summary

The project was started in the year 2011 and after completion of the first year of the project in the year 2012 the second phase started in the year 2014-15. The collaborating institutes/universities in the project were Jawaharlal Nehru University, New Delhi; University of Maryland, USA; Khulna University, Bangladesh and Indian Institute of Science, Bangalore.

The main purpose of the research was to facilitate the assessment of regional impacts of climate change and anthropogenic pressure on the ecosystem dynamics of the Sundarban mangrove in Indian and Bangladesh and communicate these results to local stakeholders.

The project has enabled in the preparation and documentation of various biogeochemical processes in the mangrove environment of Sundarban in both India and Bangladesh and provides sufficient results to be used by stake holders for policy intervention and proper management.

Keywords

Mangroves, Biogeochemistry, Nutrients, Trace metals, Anthropogenic

Objectives

The main objectives of the project were:

1. Characterize dissolved and solid nutrient pools spatially and temporally to evaluate anthropogenic impacts on nutrient biogeochemical processes.
2. Apportion nitrogen and organic pollutant sources and their release time based on mass accumulation rates calculated from 210Pb and 137Cs dating.
3. Apply bulk, stable isotopes (C, N, O, and S) and molecular tracers to explore historical changes in the nutrient biogeochemical dynamics.
4. Track sources and cycling of pollutants by using fluorescence spectroscopy and geochemical modelling.
5. Develop a regional earth system modelling framework to depict the status of ecosystem for sustainable management.

Amount received and number years supported

The Grant awarded to this project was:

US$ 45,000 for Year 1: 2011-12

US$ 45,000 for Year 2: 2014-15

Activity undertaken

1. Field work was conducted to undertake samples. Surface sediments, core sediments and surface water samples were collected to fulfill the objectives of the project.
2. Preparation of interactive multi-media CD-ROMs with the comprehensive technical reports with digital database, maps and other information.
3. Presentation of the project activities and finding of the study in the various workshops/seminars/conferences to help to create wider awareness.

Results

1. A documentation of trace metals, sedimentary nutrients and elemental and isotopic composition of C and N was generated for the Sundarban mangrove ecosystem of India as well as Bangladesh.
2. The project led to the award of one PhD degree on biogeochemical processes in the Sundarban mangrove.
3. One scientific publication already achieved and the other two are under revision.
4. Preparation of digital repository of dataset for the Sundarban mangroves as a whole.

Relevance to the APN Goals, Science Agenda and to Policy Processes

The proposed research being related to the APN's Strategic Goal "*Supporting regional cooperation in global change research on issues particularly relevant to the region*" focused to facilitate the assessment of regional impacts of climate change and anthropogenic pressure on the ecosystem dynamics of the Sundarban mangrove in India and Bangladesh (**APN's Science Agenda: 1 and 2**). The research objectives attempted to target the APN's scientific interests "*to understand the global environmental change by conducting regional research through collaboration and capacity development*". It also attempted to address the APN's goal to "*improve the scientific and technical capabilities including transfer of technology and know-how within the region*". Therefore, the results and information generated is meant to be shared among the participating scientists as well as the countries and will also be kept under public domain through relevant publications to be used by relevant policy makers for developing an integrated management framework for conservation of the Sundarban mangrove ecosystem.

Self-evaluation

Given the time frame of the project the objectives seemed achievable to some extent but due to the bureaucratic hurdle as a result of volatile political situation in the Bangladesh which covers maximum part of the Sundarban, it was a challenge to attain all the results in the remaining time after the field work was conducted. We have tried our best to incorporate most of the results that were primarily needed to fulfill the major objectives of the project which will help policy makers for developing a management framework for conservation of Sundarban mangrove ecosystem.

Potential for further work

1. Development of institutional capacity strengthening by advanced on-the-job training to the participants of the collaborating institutions and agencies.
2. Preparation of data inventory for future research.
3. Developing a decision support system for policy makers and managers.
4. Involvement of stakeholders and dissemination of knowledge gained through database analysis, to strengthen policy and planning within relevant agencies, and to inform research institutions and the public, nationally and regionally.

Publications (please write the complete citation)

1. M.B.K. Prasad, Alok Kumar, Dilip K Datta, **AL. Ramanathan** (2014). **Spectrofluorometric analysis of organic matter in the Sundarban mangrove, Bangladesh. Indian Journal of Geomarine Sciences, 43 (6), 999-1006.**
2. Alok Kumar and AL. Ramanathan (2014). **Speciation of selected trace metals (Fe, Mn, Cu And Zn) with depth in the sediments of Sundarban mangroves: India And Bangladesh. Journal of Soils and Sediments. (Under revision).**

Acknowledgments

Preface

The study highlights the status of nutrients, trace metals and Organic matter and their driving forces behind the nutrient dynamics ad biogeochemical variability in the Sundarban mangrove ecosystem. Global climate change and coastal urbanization have altered structure and function of mangroves which are the tropical coastal forests that regulate marine biogeochemistry, by transporting nutrients and energy along the land-ocean continuum and the linkage between man–ecosystem. The Sundarban, the World's largest single-block mangrove in the Gangetic delta of India and Bangladesh, is highly vulnerable to increasing urbanization and climate change. Therefore, an integrated assessment of ecosystem function with nutrient biogeochemical processes and material accretion rates is required to delineate driving forces behind coastal environmental changes that helps in designing sustainable management policies to protect mangroves for future generations.

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1.0 Introduction

Mangrove environment supports important biogeochemical functions and services besides economic and cultural functions (Primavera, 1997; Rönnbäck et al., 2007; Birch et al., 2012) and have high ecological significance as well (Nagelkerken et al., 2000; MacFarlane et al., 2007). The biogeochemical functions of mangrove include primary production, sedimentation, nutrient cycling, succession, biomass, litter dynamics and organic matter OM dynamics etc (Alongi et al., 1992; Mitsch and Gosselink, 2000; Kristensen et al., 2008). Mangroves also act as physical and biogeochemical barrier for pollutants from agricultural runoff, industrial effluents and domestic sewage as they help in accumulation and partitioning of trace metals in the rhizosphere (Huerta-Diaz and Morse, 1992; Marchand et al., 2011; Qiu et al., 2011; Zhou et al., 2011). However, such environments are vulnerable to anthropogenic stress and mangrove habitats are worst affected as they protect the integrity of marine systems at the interface of land and ocean (Harbison, 1986; Bayen, 2012). Significant research has been undertaken on the biogeochemistry of tropical mangrove ecosystem in the last decade on the other hand severe destruction of mangrove cover has also taken place in last few decades owing to urbanization and anthropogenic pressures (Black and Shimmield, 2003). Increased human activities such as damming or land use change in the coastal environment due to agriculture and aquaculture have led to the loss and deterioration of mangroves (Alonso-Pe´rez et al., 2003; Farella et al., 2001; Yang et al., 2007). Keeping these facts in picture there is a need to understand the tropical mangrove forest ecology and biogeochemistry to overcome the practical challenges that may arise in future as a result of human perturbations. The main objectives of the project were,

1. Characterize dissolved and solid nutrient pools spatially and temporally to evaluate anthropogenic impacts on nutrient biogeochemical processes.
2. Apportion nitrogen and organic pollutant sources and their release time based on mass accumulation rates calculated from ^{210}Pb and ^{137}Cs dating.
3. Apply bulk, stable isotopes (C, N, O, and S) and molecular tracers to explore historical changes in the nutrient biogeochemical dynamics.
4. Track sources and cycling of pollutants by using fluorescence spectroscopy and geochemical modelling.
5. Develop a regional earth system modelling framework to depict the status of ecosystem for sustainable management.

These results will address the overall ecosystem dynamics in relation to impacts of climate change and human pressure on mangroves. Thus, protecting these environments is imperative for maintaining socio-ecological diversity and sustainable development of nature.The outcome of such studies will further help us in undertaking better management practices for the sustainable development of Sundarban mangroves.

2.0 Methodology

In order to understand the biogeochemical processes in the inter-tidal mangrove ecosystem of Sundarban it was imperative to analyse all major components e.g. nutrients, trace metals, elemental and isotopic composition. A total of seven sediment samples were collected three from Indian Sundarban (IS) mangroves transect along river Bidya and four from Bangladesh Sundarban (BS) transect along river Passur using stainless steel auger of 1.5m length and 7cm inner diameter. The collected core samples were immediately transported to the field laboratory where they were sectioned at 5 cm interval. The maximum length of the core collected varied between stations (maximum depth of 45 cm) due to different nature of substratum. The core sections were collected and packed in a pre-cleaned polythene bags and stored at 4° C until analysis. The samples were freeze-dried, finely powdered and homogenized for metal extraction. The surface water samples were analysed for DOC, bicarbonate, dissolved inorganic phosphate and dissolved organic matter

content. The depth-wise seven core sediment samples up to a depth of 45 cm were analysed for nutrients (e.g. C, N and P), trace metals (Al, Cd, Cr, Cu, Fe, Mn, Pb, Zn) and isotopes ($\delta^{13}C_{org}$ and $\delta^{15}N$).
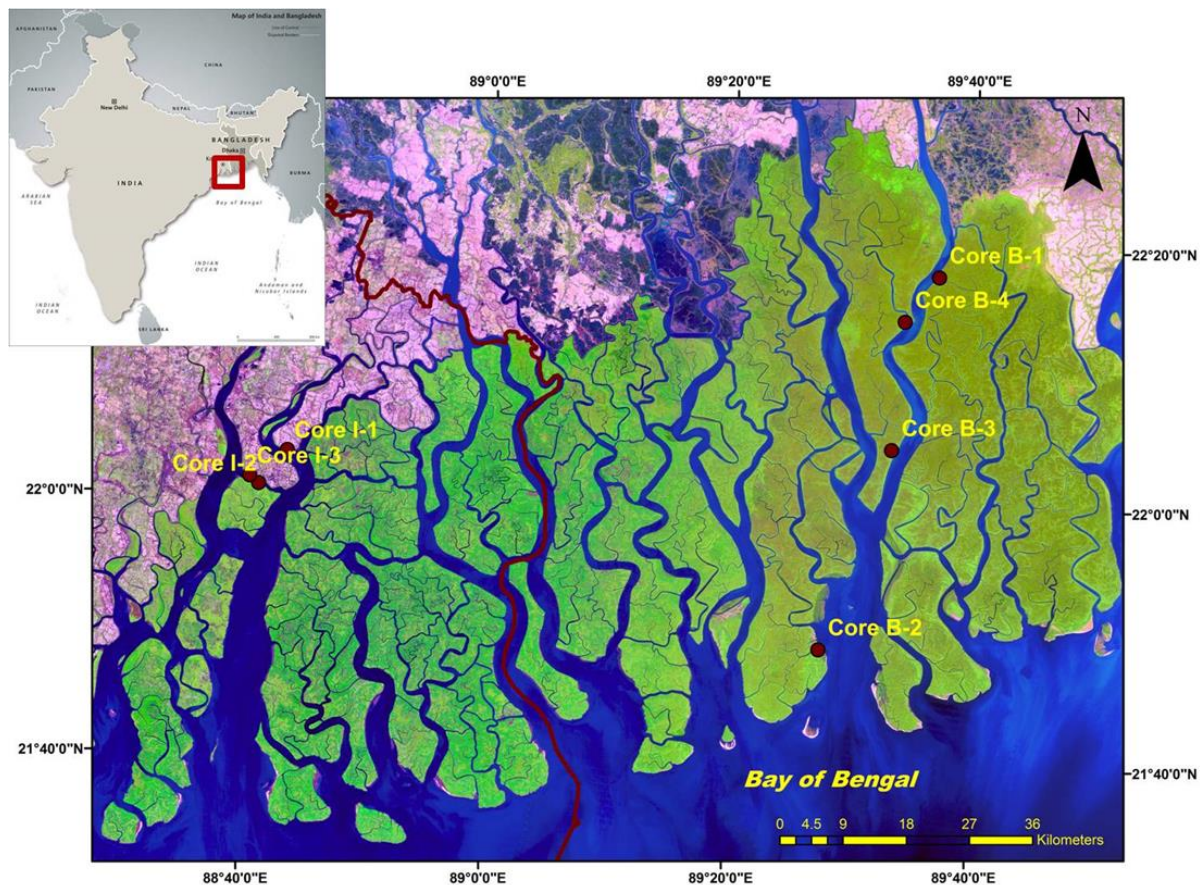

Figure 1: Study area with sediment core location in Indian (I-1, I-2, I-3) and Bangladesh (B-1, B-2, B-3, B-4) part of Sundarban

The Sundarban is the largest delta in the world formed by Ganges and Brahmaputra rivers and is occupied by the largest single block of littoral mangrove ecosystem distributed over an area of 10,200 km2 (**Fig. 1**). Geographically Sundarban lies between latitudes 21° 31' N and 22° 30' N and between longitudes 89° 01' E and 90° 18' E (Katebi, 2001; Islam, 2003). A majority of 60% of this forest is found in Bangladesh (40% in India), where it is protected as the Sundarban Reserve Forest, which is both a Ramsar site, since 1992, and a World Heritage site of the United Nations Educational, Scientific and Cultural Organization (UNESCO) since 1997. The G-B delta plain is a tideinfluenced depositional system comprising of a complex network of estuaries and islands dissected by innumerable tidal channels. The delta floor is dominated with quaternary sediments eroded from the highlands carried and deposited by Ganges, Brahmapura and Meghna rivers and their distributaries supplemented with marine salt and clay from the Bay of Bengal (Umitsu, 1997; Islam, 2001). Sundarban landform is a complex network of thousands of creeks and river channels which brings with them tons of sediments carrying terrestrial load which gets deposited in the mud flats, mangrove swamps and salt flats. These landforms are suitable sites for the propagation of mangrove propagules which grow to provide coastal protection in the form of barrier between land and sea (Selvam, 2003). With respect to vegetation, *Heritiera fomes* (Sundari) from which Sundarbans take its name, *Excoecaria agallocha* and others include *Bruguiera species, Ceriops decandra, Sonneratia apetala, Xylocarpus species, Avicennia species, Aegialitis rotundifolia, Rhizophora apiculata and*

Rhizophoraceae are of minor importance. Other species include *Carapa obovata, Phoenix paludosa, Nypha fruticans* (Karim 1995).

Over the years, Sundarban mangrove ecosystem has undergone degradation owing to anthropogenic activities e.g. ports, ship breaking, tourism, fishing, aquaculture etc. (Hussain and Acharya 1994). Rapid changes with respect to, land use pattern, effluent discharges from aquaculture ponds, reduction in freshwater and run-off from agricultural fields and oil spill from ports have seriously affected the biodiversity and biogeochemical processes in the Sundarban (Erwin 2009; Rahman et al. 2009). In Bangladesh Sundarban, south flowing rivers are quite active while in the western Indian part tidal flow dominates over riverine.

Instruments

Metrhom TOC analyzer was used for DOC analysis. HACH DR2700 spectrophotometer was used for spectrophotometric analysis. A microwave digestion system (*MARS 5; CEM Corp, Matthews, N C*) was used for sediment digestion. Inductively coupled plasma mass spectrometry (*Agilent Technologies, Tokyo, Japan*) ICPMS was used to determine trace metal concentration. For elemental analysis CN elemental analyzer (*Model: CN Analyser Eurovector EA 3000*) was used. Stable carbon isotopes and nitrogen isotopes were measured using *Thermo Finnigan Delta plus mass spectrometer* after high temperature combustion in a *Flash EA 1112* elemental analyzer.

Chemicals and solutions

All the reagents used were of analytical reagent grade (Merck). All the solutions were prepared with deionized water (*Milli Q Plus system; Millipore, Bedford, MA*) with 18.2 MΩ/cm resistivity. All of the standard solutions were standardized and kept at 4°C in darkness until use. Dilutions of these standard solutions were prepared daily for the analyses. Concentrated nitric acid (HNO_3; Mallinckrodt Chemicals, USA) and concentrated hydrochloric acid (Merck) were used for the aqua-regia digestion method. Concentrated 35% HCl (Merck), 30% H_2O_2 (Merck), Acetic acid (Merck), Hydroxylammonium chloride (Merck), Ammonium acetate (Merck) and tetra-Sodium Pyrophosphate (decahydrate) (Merck) were analytical reagent grade. Sediment standard reference material with certified concentrations for individual metals was used. NIST SRM 2711 (Montana soil) was used to validate our results. The analytical results of trace metals in Montana soil indicated that the observed values are very close to the certified values.

Sediment standard reference material with certified concentrations for phosphorus was used. NIST SRM 1646a (Estuarine sediment) was used to validate our results. The precision and bias assessed by the reagent blanks and replicate samples were <5% of the mean analytical concentrations for all of the elements. The recovery rates in the standard reference material (NIST SRM 1646a) for all of the measured elements were around 95–105%.

Trace metal analysis

The EPA 3051 method was used for sample digestion (method 3051; USEPA 1997). The freeze-dried and finely powdered sediment sample (0.2–1.0 g) was weighed into a dry, clean Teflon digestion vessel and 5 ml of aqua-regia was added. The microwave conditions for digestion were: stage 1: microwave power 1200 W, 300 PSI, and ramp for 2 min; stage 2: microwave power 1200 W, 300 PSI, and ramp for 3 min followed by a 5-min hold. After cooling for 30 min, the vessels were opened carefully. Each digestion solution was transferred to a 50-ml volumetric flask, diluted to the mark with MilliQ water, filtered through a Millipore membrane (0.45 μm), and kept in a polypropylene bottles for analysis (Rahman et al., 2009).

Grain size analysis

Laser particle analyzer *Microtrac S 3500* was used for sediment grain size analysis. For grain size analysis the sediments were pre-treated using 30% H2O2, boiling with 10% HCl and tetra-Sodium Pyrophosphate (decahydrate) was added (Konert and Vandenberghe, 1997). All the samples were run in triplicates and the average value was considered.

Total Organic Carbon (TOC) analysis

Rapid titration method was used for total organic carbon analysis (Walkey-Black, 1934).

Total Sedimentary Phosphorus (TSP)

TSP in each sample was determined by wetting sediment samples with 1M $Mg(NO_3)_2$ solution and combustion at 550°C for 2 hours. Samples were cooled to room temperature then agitated and extracted in 1 M HCl for 16 hours at 25°C (Solorzano and Sharp, 1980; Cembella et al., 1986; Zhang et al., 2004). The liberated orthophosphate in the extracts was determined by spectrophotometric phosphomolydenum blue method (Zhang et al., 1999a) using *HACH DR 2700* spectrophotometer.

Pigments

Pigments were extracted for 2 minutes by ultra-sonication in HPLC-grade acetone (2 ml/g sediment) and stored overnight in frozen condition. After filtration (0.02 µm), chlorophyll (Chl) was analyzed colorimetrically on a Perkin Elmer lambda-35 spectrophotometer following the method by Dere et al. (1998; absorbance measured at 470, 645, and 662 nm). The pigment concentrations were calculated as (Lichtentaler et al., 1985)

$$Chl\text{-}a = 11.75 \; A_{662} - 2.350 \; A_{645} \qquad (1)$$

$$Chl\text{-}b = 18.61 \; A_{645} - 3.960 \; A_{662} \qquad (2)$$

$$Total \; carotene = 1000 \; A_{470} - 2.270Ca - 81.4Cb/227 \qquad (3)$$

Where, Chl-a and Chl-b are Chlorophyll-a and Chlorophyll-b respectively. Typical precision of duplicate runs was ≤ 2%.

Bulk Properties (C_{org}%, TN%, $\delta^{13}C_{org}$‰, $\delta^{15}N$‰)

Sediment samples were air dried and homogenised for elemental and isotope analysis. In order to estimate Corg, 25-30 mg and for δ^{13}Corg, 2-5 mg of sediment was taken in a silver boat and approximately 150µL of 1N HCl was added to silver boat and kept at 40°C for 24 hours in order to remove inorganic carbon. Total nitrogen (TN) was measured without any acid treatment using c.a. 25-30 mg of sediment sample and $\delta^{15}N$ was measured taking approximately 50 mg of sediment sample in a tin boat. Corg% and TN% were measured using CN elemental analyzer (*Model: CN Analyser Eurovector EA 3000*). The relative standard deviation (RSD) for sediment samples was <5% and <1% for C and N respectively. Stable carbon isotopes and nitrogen isotopes were measured using *Thermo Finnigan Delta plus mass spectrometer* after high temperature combustion in a *Flash EA 1112* elemental analyzer and the results were expressed using the equation:

$$\delta^{13}C(\text{‰}) = \frac{[R_{sample} - R_{standard}]}{[R_{standard}]} \times 1000 \qquad (4)$$

Where R= $^{13}C/^{12}C$ or $^{15}N/^{14}N$. Vienna Pee Dee Belemnite (V-PDB) standard was applied for Corg with a reproducibility of <0.1‰ and Acetanilide for C and TN analysis (OAS 164195). Atmospheric N_2 was used as standard and peptone was used an internal standard after every seventh sample.

3.0 Results & Discussion

Estuaries, mangroves and coastal wetlands are sites for nutrients loading of anthropogenic origin in recent decades (Moutin et al., 1993; Marques et al., 1997; Gomez et al., 1999; Cardoso et al., 2002; Dolbeth et al., 2003; Coelho et al., 2004). Mangroves occupy nearly 75% of the world's tropical and subtropical coastline and are highly productive ecosystems (Alongi, 1996; Farnsworth, 1998; Marchand et al., 2006). Phosphorus plays a key role in global biogeochemical cycles and is an essential nutrient limiting marine productivity (Sanudo-Wilhelmy et al., 2001; Babu and Nath, 2005; Hou et al., 2009; Abdallah, 2011). The sorption of phosphate on sediments has a major influence on transport, degradation, and ultimate fate of phosphorus in marine ecosystems (Zhuang et al., 2014). Phosphorus release from sediments determines concentration of phosphates in the overlying water and has significant impact on coastal eutrophication. Phosphorus cycling and bioavailability depends not only on total phosphorus but the forms in which P is readily available for biological growth (Psenner and Puckso, 1988; de Jonge and Villerius, 1989; Lebo, 1991; Ruttenberg, 1992; Jensen and Thamdrup, 1993; Paludan and Morris, 1999; Andrieux-Loyer and Aminot, 2001; Coelho et al., 2004).

TSP in different sediment cores ranged as I-1, 9.83-10.76 µmol/g (10.32±0.28); I-2, 10.12-11.20 µmol/g (10.66±0.32); I-3, 8.36-9.40 µmol/g (8.80±0.37); B-1, 8.80-11.30 µmol/g (10±1); B-2, 11-11.40
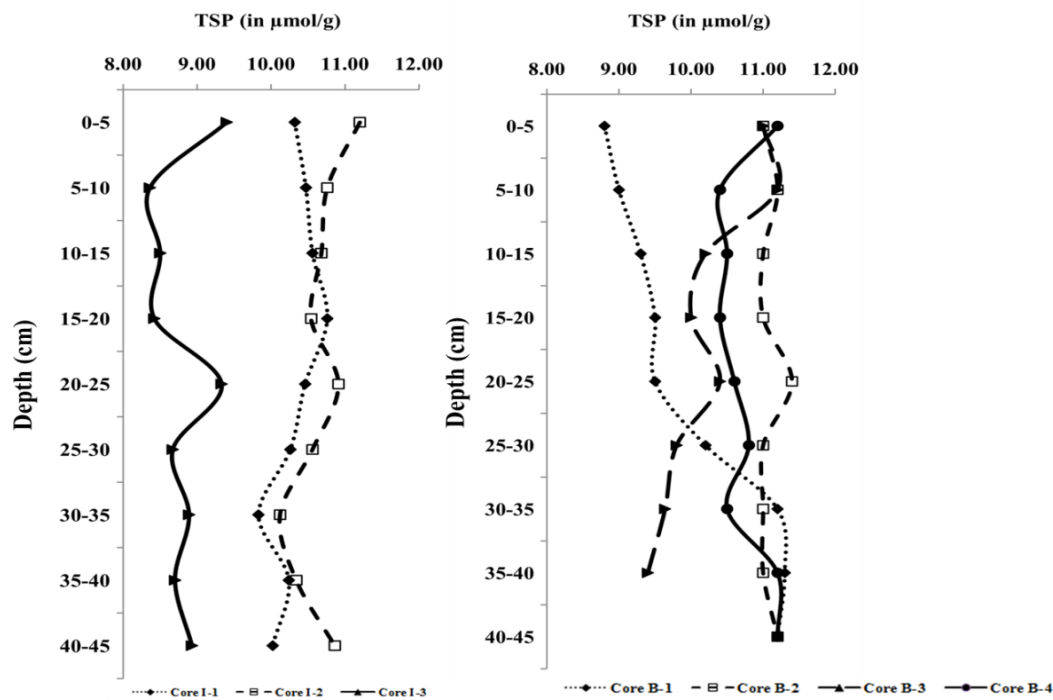

Figure 2: Total sedimentary phosphorus variations in sediment cores I-1, I-2, I-3 (Indian Sundarban) and B-1, B-2, B-3, B-4 (Bangladesh Sundarban)

µmol/g (11.09±0.15); B-3, 9.40-11.20 µmol/g (10.21±0.54); B-4, 10.40-11.20 µmol/g (10.76±0.35) (**Fig. 2**). TSP in the Sundarban sediments falls well within the limits of global average for mangroves i.e. 3.22-51.61 µmol/g (Alongi et al., 1992). Furthermore, TSP exhibited little change with depth and followed irregular trends. No significant and consistent trend with changing salinity was observed rather high mean TSP was observed in high salinity samples. Pore water mean pH varied between 6.14-6.63 for IS and between 6.31-6.66 for BS (**Fig. 3 and 5**). For pH no apparent and consistent variation was observed with depth. The mean phosphate concentration ranged as I-1, 0.01 mmol/L; I-2, 0.02 mmol/L; I-3, 0.01 mmol/L; B-1, 0.02 mmol/L; B-2, 0.02 mmol/L; B-3, 0.01 mmol/L; B-4, 0.003 mmol/L. There was no clear trend in pore water concentration with depth as well as salinity.
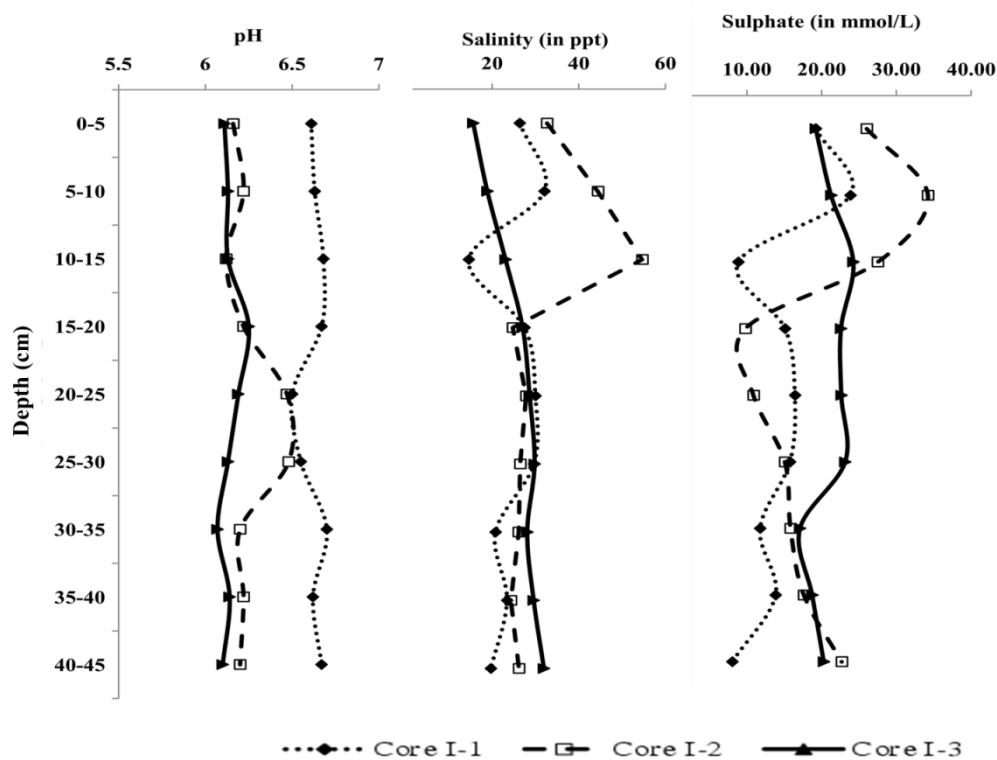
Figure 3: Depth wise variation in pore water pH, Salinity (ppt) and Sulfate (mmol/L) in Indian Sundarban

Mean salinity values observed for different cores were I-1, 24.89 ppt; I-2, 31.93 ppt; I-3, 25.86 ppt; B-1, 2.28 ppt; B-2, 21.66 ppt; B-3, 14.90 ppt; B-4, 2.43 ppt (**Fig.3 and 4**). No apparent TSP distribution pattern was observed with salinity. The pore water mean sulfate concentration varied between 14.75-21.01 mmol/L in IS and 5.12-18.12 mmol/L in BS (**Fig. 3 and 4**). Pore water sulfate concentrations increased along the salinity gradient and again no apparent difference in concentration and trend was observed with depth.

Higher nutrient concentration was observed in the surface water of IS than BS leading to the presence of high DOC in IS than BS (**Fig. 4**). Presence of higher OM content in fine-grained sediments can result in fermentation, which leads to breakdown of complex organic compounds and contribution of OM to the DOC pool (McMahon and Chapelle, 1991; Routh et al., 1999). Variation in DOC concentrations between the different sites in mangrove forests is probably influenced by dominant mangrove species in the specific area. The high variability in DOC probably results from mixing of different types of waters, bioturbation (burrowing activity), redox changes, and variable litter decomposition.
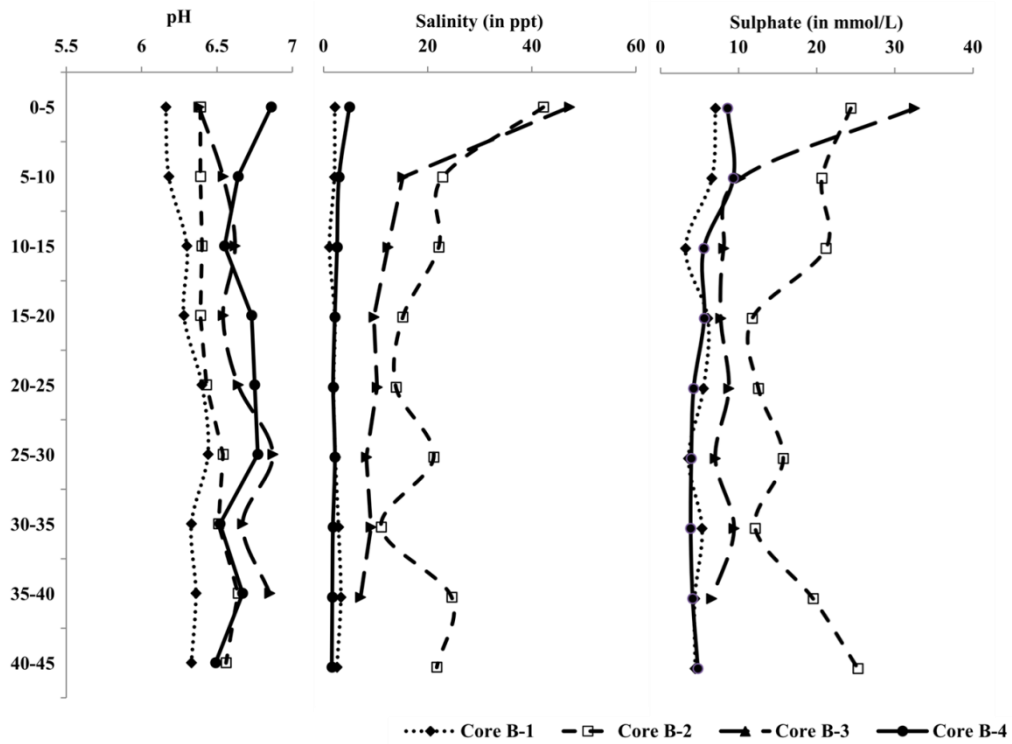
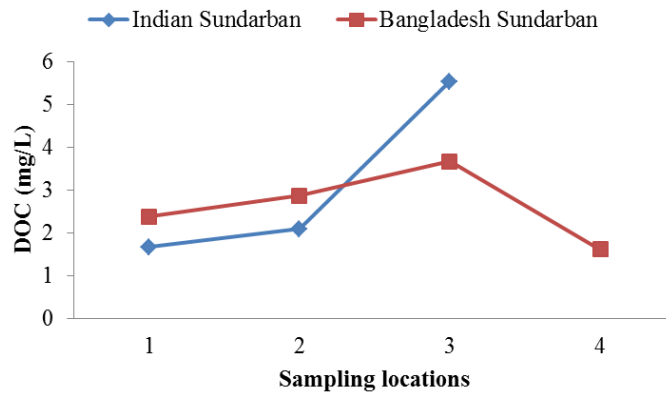**Figure 4**: Depth wise variation in pore water pH, Salinity (ppt) and Sulfate (mmol/L) in Bangladesh Sundarban

Figure 5: Dissolved organic carbon (DOC) variation in surface water of Sundarban mangroves

Pigments

Distribution of Chl a, Chl b, and total carotenoid concentrations are shown in figure 6 and 7. Concentration of pigments is less in the Bangladesh sediments than Indian Sundarban sediments. This is most likely due to various factors such as low phytoplankton biomass (Kathiresan, 2000), degraded litter input and photo-oxidation. In contrast, high productivity and sharp demand for oxygen make mangrove systems eutrophic (Marchand et al., 2006). Previous studies indicate that pigments are better preserved in eutrophic environments (Leavitt and Hodgson, 2001 and references therein) which can be the reason in case of Indian Sundarban which are more eutrophic than Bangladesh Sundarban as depicted by the nutrient studies. However, the down core pigment distributions indicate irregular trends characterized by decrease with depth. This is probably related to differences in grain size, effect of bioturbation, and microbial decomposition of OM. Pigments concentrations also vary depending on mangrove species, depositional environments, and seasonality (Oswin and Kathiresan, 1994; Behera and Choudhury, 2002).
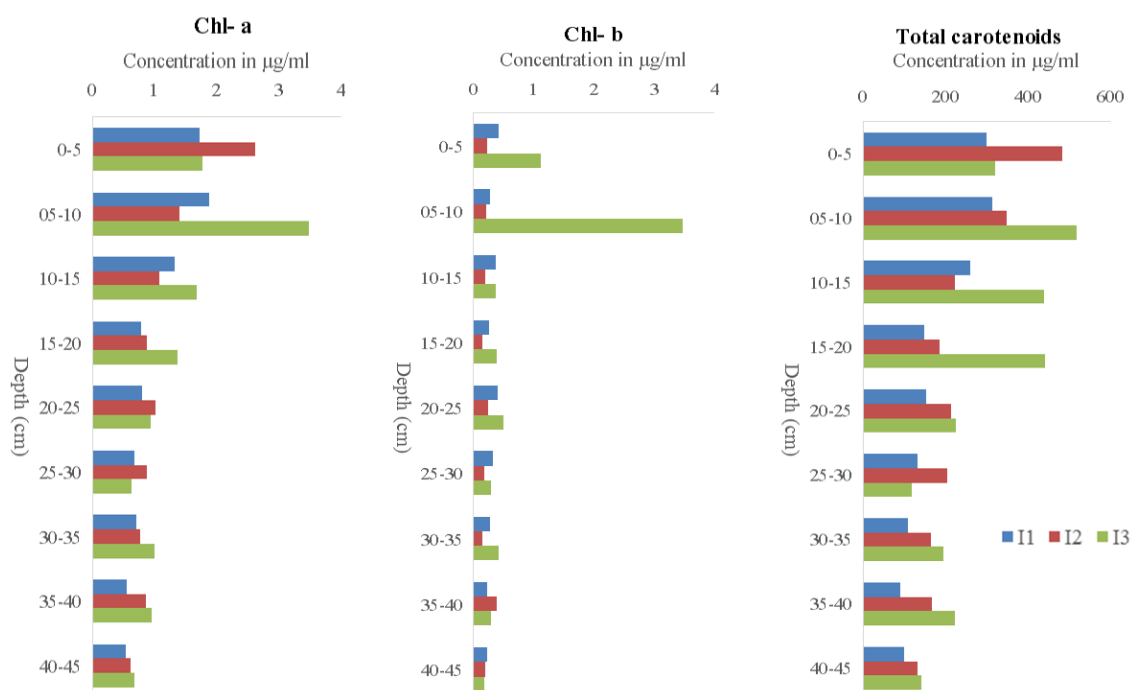

Figure 6: Pigments (Chl-a, Chl-b and Total carotenoids) content in the core sediments of Indian Sundarban
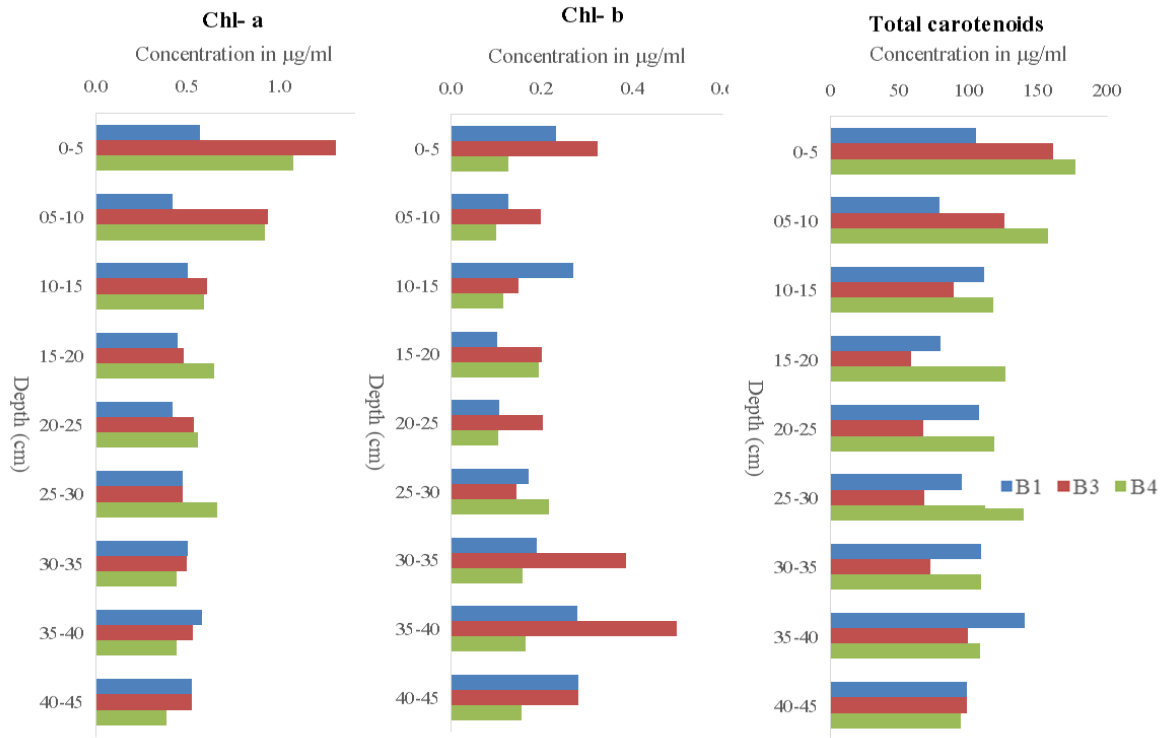
Figure 7: Pigments (Chl-a, Chl-b and Total carotenoids) content in the core sediments of Bangladesh Sundarban
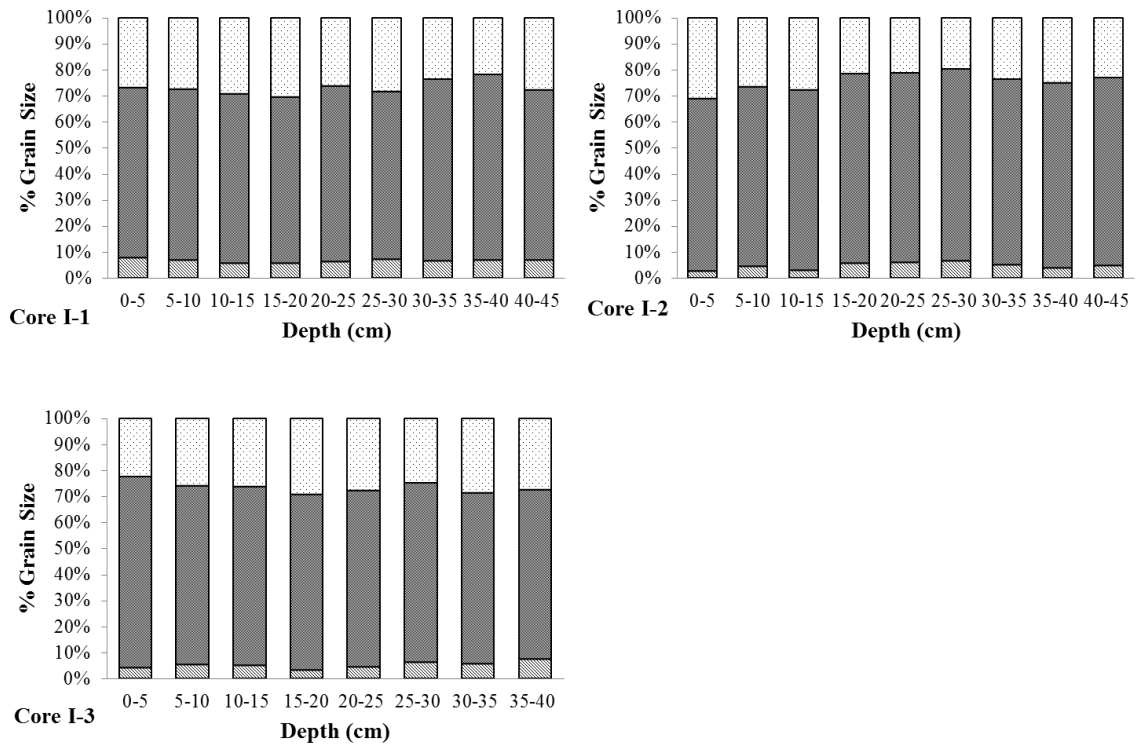
Figure 8: Textural characteristics of the core sediments (I-1, I-2 and I-3) of Sundarban mangrove, India
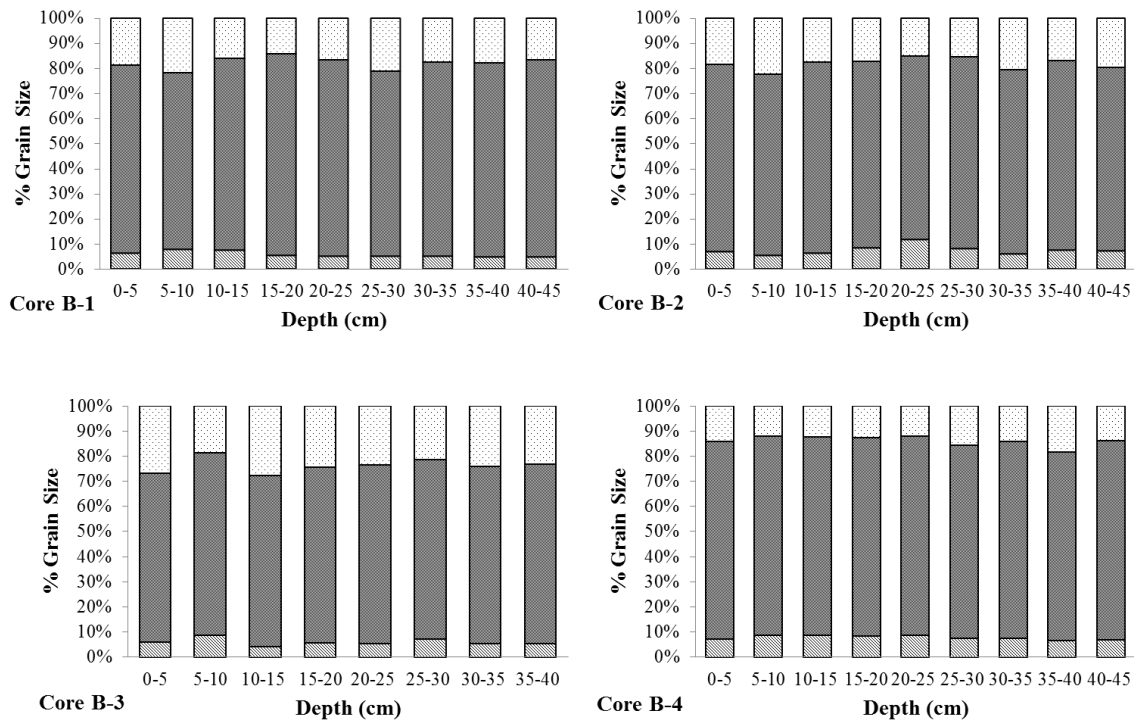
Figure 9: Textural characteristics of the core sediments (B-1, B-2, B-3 and B-4) of Sundarban mangrove, Bangladesh

Sediment texture analysis is an efficient tool to differentiate various depositional environments of a region (Perjup, 1988; Flemming, 2000). The grain size composition of Sundarban mangrove sediments followed the order Silt>Clay>Sand (**Fig. 8 and 9**). The %sand content in the Indian Sundarban (IS) ranged from 2.46-7.62% and in Bangladesh Sundarban (BS) higher %sand content was found which ranged from 3.93-11.51% similarly, there was dominance of silt fraction in BS than IS which ranged from 67.20-80.63% and 64.14-73.92% respectively, indicating dominance of high energy conditions (Massolo et al., 2012) in BS than IS. Higher % clay content was found in the IS (19.60-31.22%) compared to BS (12.11-27.74%) suggesting prevalence of low energy areas of suspensional deposits in IS than BS.

The %OC content in the Sundarban mangroves is lower than the average reported for mangrove sediments (5 DW% Corg) (Bouillon et al. 2000; Gonneea et al. 2004; Chatterjee et al., 2009). The low %OC may be the result of rapid tidal export of locally produced organic matter to the coastal zone (Rogers et al., 2013).

In IS core sediments, the mean concentration of various trace metals were Al, 1.61%; Fe, 4.50%; Mn, 609.92 µg/g; Cu, 46.92 µg/g; Zn, 71.60 µg/g; Pb, 20.79 µg/g; Cr, 72.20 µg/g; and Cd, 0.06 µg/g whereas in BS core sediments they were Al, 1.52%; Fe, 3.63%; Mn, 544.31 µg/g; Cu, 31.40 µg/g; Zn, 54.05 µg/g; Pb, 16.06 µg/g; Cr, 63.33 µg/g and Cd, 0.07 µg/g (**Fig. 10 and 11**). The mean concentrations of trace metals in IS and BS were compared with the world average Upper continental crust (UCC) (Taylor and Mclennan, 1985, 2009) and average shale (Turekian and Wedepohl, 1961) values (**Table. 1**).

Trace metals may enter into the coastal environments from different sources including natural weathering processes, anthropogenic or human activities (Sadiq et al., 1992; Badr et al., 2009 and references therein). A number of activities like fishing, ferry services, brick manufacturing, sewage drainage and other industrial activities (e.g. power plants) and commercial activities like intensive use of mechanised boats for tourism and aquaculture ponds etc. have been reported to be an important source of trace metals in the IS (Sarkar et al., 2007; Chatterjee et al., 2007; Chatterjee et al., 2009; Banerjee et al., 2012). In BS, core B-3 exhibits maximum contamination due to its location
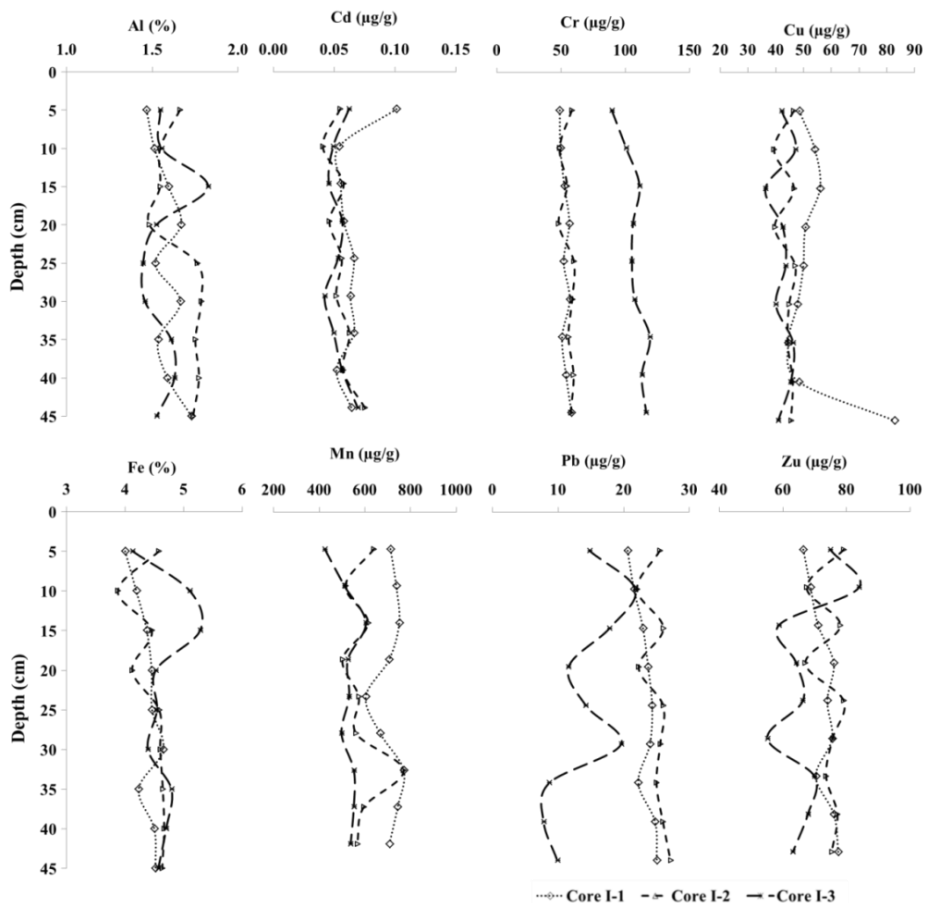
Figure 10: Depth profile of trace metals (Al and Fe concentration in % and other trace metals in µg/g) in the core sediments of Indian Sundarban mangrove ecosystem

being crossed by tributaries from the polluted Sibsa river which brings a considerable pollutant load as it passes through the industrial town of Khulna where exists abundant industrial and commercial activities like ship breaking and repairing activities of Khulna Shipyard and boat and barge building, fish processing unit discharge their effluent into the Rupsha River (Khan et al., 2007; Rahman et al., 2009; Ahmed et al., 2011). Khulna newsprint mill, Goalpara power plant, jute, hardboard and steel mills also discharge their untreated wastes into Bhairab river (Ahmed et al. 2003).

In Sundarban as a whole the Cu, Pb and Zn concentrations were lower than most mangroves world over while Cr concentration exceeded the many mangroves world over. Trace metals Fe and Mn exhibit fairly similar distribution pattern suggesting diagenetic processes and strong association between the two elements in the geochemical matrix.

Estimation of Pollution Status

A number of indices have been used to quantify trace metals pollution levels in sediments and their ecological risk. Previously, various authors (Salomons and Förstner, 1984; Müller, 1969; Hakanson, 1980) have proposed pollution indices to convert calculated numerical results into broad descriptive bands of pollution ranging from low to high intensity. In the present study, Enrichment Factor (EF) was used to estimate the pollution status of Sundarban mangroves. In both the indices pre-civilization background levels are required to compare the present day metal levels and in these two indices we have used both UCC values and shale values for CF and EF respectively.

EF values are shown in **Fig. 12 and 13**, and they were found to be principally higher than 2 for all trace metals except Cd in both IS and BS. In IS core I-1 showed significant enrichment w.r.t. Cu and Pb whereas for core I-2 only Pb was significantly enriched while in case of core I-3 Cr showed

consistently significant enrichment. In BS core core B-1, B-2 and B-3 are significantly enriched w.r.t. Pb while B-3 and B-4 are significantly enriched for Cu and Cr respectively. Over all in both IS and BS all other trace metals showed moderate enrichment (except Cd).

The study explains that a number of processes as adsorption, occlusion, co-precipitation, substitution, organic complexation and microbial fixation were controlling the distribution of trace metals in the Sundarban mangrove sediments. Lithology and mineralisation besides anthropogenic activities were important factors influencing the distribution of trace metals (Kumar et al., 2010). The comparative account of trace metals suggests that Indian Sundarban mangroves stand more polluted than the Bangladesh but overall mangrove sediments acts as trap for the studied trace metals (Lacerda, 1998; Nobi et al., 2010).
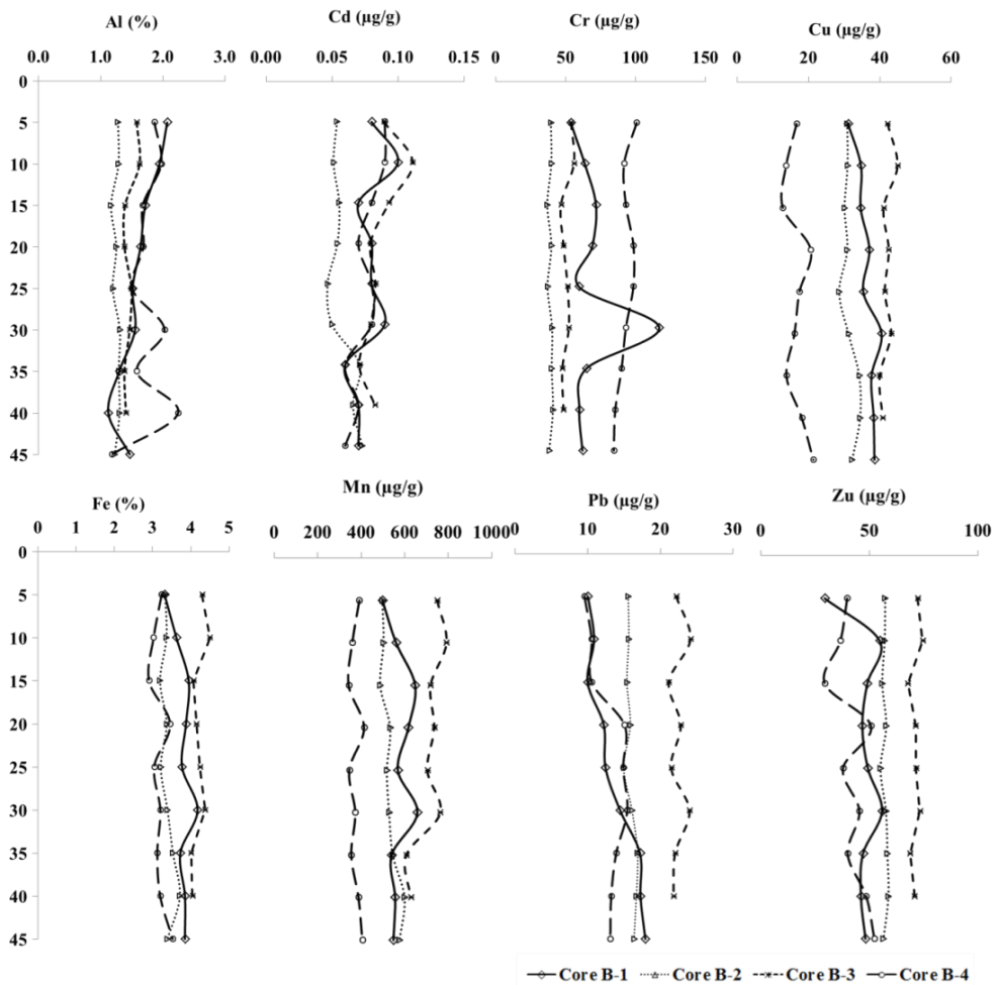

Figure 11: Depth profile of trace metals (Al and Fe concentration in % and other trace metals in µg/g) in the core sediments of Bangladesh Sundarban mangrove ecosystem
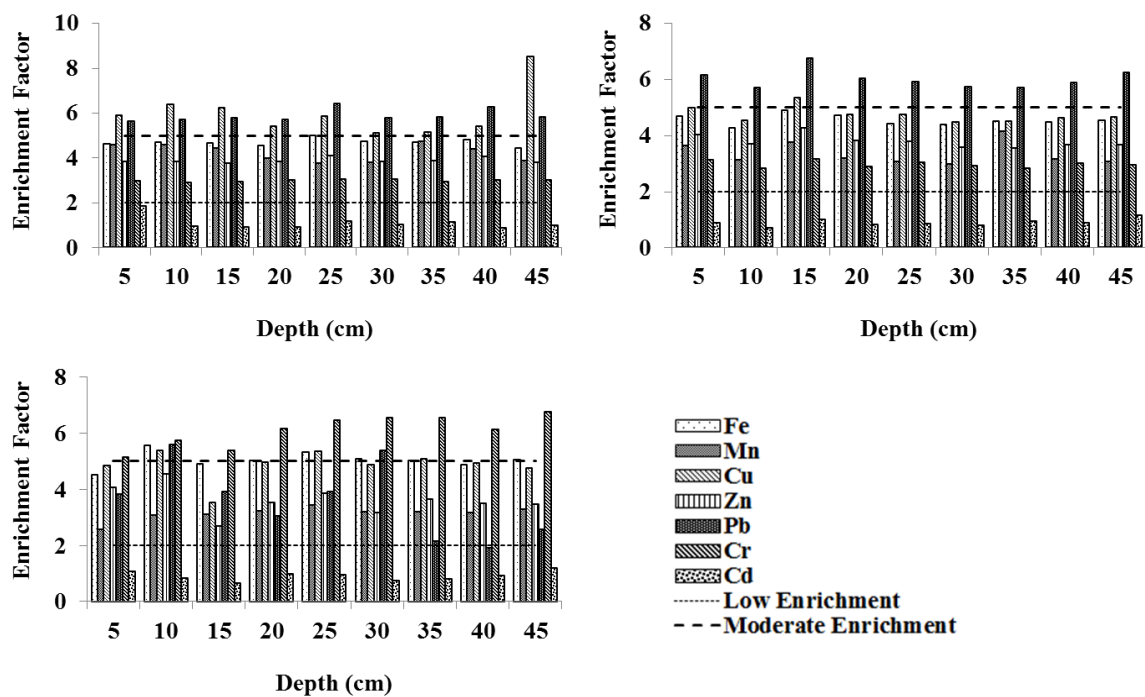
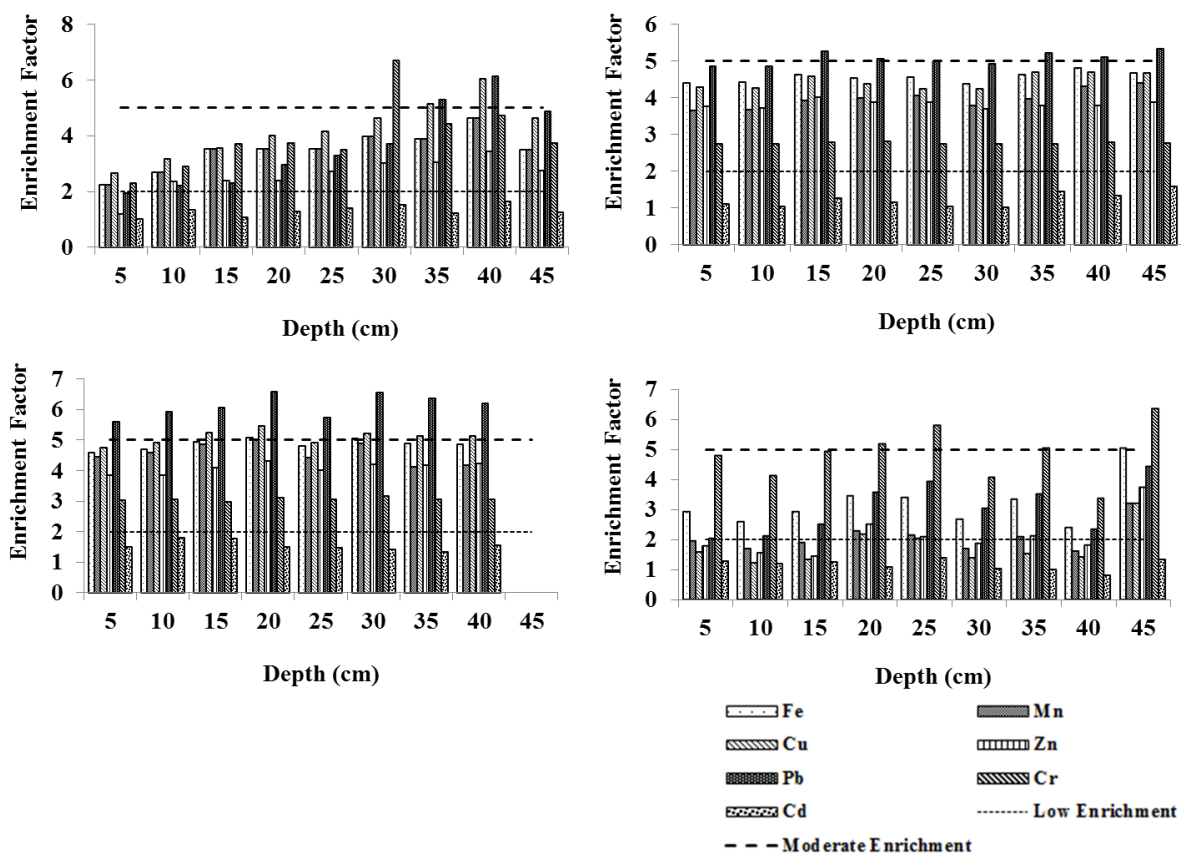**Figure 12:** Enrichment Factor (EF) in the core sediments of Indian Sundarban mangrove ecosystem

Figure 13: Enrichment Factor (EF) in the core sediments of Bangladesh Sundarban mangrove ecosystem.

Table 1: The minimum, maximum and average concentrations of trace metals (mg/kg except Fe and Al) in the collected samples from Sundarban mangrove sediments in this study and some mangrove wetlands around the world (modified from Usman et al., 2013)

Locations	Trace metals									References
	Al	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**	
India	**1.45-1.83**	**0.04-1.0**	**48.20-119.61**	**36.30-82.25**	**3.88-5.28**	**424.11-770.58**	**-**	**7.81-25.06**	**55.15-83.95**	**This Study**
Bangladesh	**1.12-2.24**	**0.05-.11**	**36.92-117.07**	**12.85-44.96**	**2.91-4.50**	**342.26-791.99**	**-**	**9.58-24.13**	**29.45-74.53**	**This Study**
Red Sea	-	ND-5.48	ND-31.4	45.5-280	-	-	ND-20.9	13.5-230	3.95-275	Usman et al., 2013
Punta Portete, Costa Rica	-	7.3	22.6	8.4	-	-	102	34.5	14.7	Guzman and Jimenez (1992)
Hainan Island, China	-	0.11	40	18	-	-	-	19	57	Qiu et al. (2011)
Shenzhen, China	-	0.136	7.97	38.3	-	537	25	28.7	11.4	Peng et al. (1997)
Mai Po, Hong Kong	-	2.62	39.2	78.5	-	-	3	79.2	240	Tam and Wong (2000)
SungeiBuloh, Singapore	-	0.181	16.61	7.06	-	-	7.44	12.28	51.24	Cuong et al. (2005)
Pichavaram, India	14.78-22.10	6.6	141.2	43.4	2.34-4.69	385-1248	38-86	11.2	93	Ramanathan et al. (1999)
Kottuli, India	-	ND-0.08	ND-0.71	0.8-244	-	6.43-29.47	0.02-1.93	2.31–23.62	218–584	Harikumar and Jisha (2010)
Cienaga Grande, Colombia	-	0.8-3.16	13.2	23.3	0.8-1.76	179-615	12.1-28.8	12.6	91	Perdomo et al. (1998)
Punta Mala Bay, Panama	-	<10	23.3	56.3	9.8	295	27.3	78.2	105	Defew et al. (2005)
Newington, Australia	-	-	-	71.3	-	-	-	121.9	229.9	MacFarlane et al. (2003)
Port Jackson, Australia	-	-	-	62-102	-	-	-	180–443	145–351	MacFarlane (2002)
Hawksbury, Australia	-	-	-	18.9	-	-	-	26.4	94	MacFarlane (2002)
Guanabara Bay, Brazil	-	1.32	42.4	98.6	4.32	-	-	160.8	483	Kehrig et al. (2003)
Mazatla, Northwest México	-	3.1-3.3	-	31.9-44.9	-	-	-	49.6–54.0	217.8–323.5	Jara-Marini et al. (2008)
Average shale	8	0.30	90	45	4.72	850	68	20	95	Turekian and Wedepohl (1961)

Organic matter characteristics

Mangrove environments are sites of intense carbon and nutrient cycling across the land ocean interface having potentially high impact on global biogeochemical cycles (Borges et al., 2003; Chmura et al., 2003; Dittmar et al., 2006; Alongi et al., 2007; Kristensen et al., 2008; Ranjan et al., 2011). Organic matter (OM) characterization in the coastal environment enables us to understand the biogeochemical transformation of OM and its influence on ecosystem productivity in response to changing environmental conditions. Isotopic composition of carbon ($\delta^{13}C_{org}$) and nitrogen ($\delta^{15}N$) have been successfully used for source apportioning and understanding the fate of OM in the coastal sediments (Middelburg and Nieuwenhuize, 1998; Raymond and Bauer, 2001; Zhang et al., 2007; Bao et al., 2013). Similarly, C_{org}/TN_{atm} ratio has been used to distinguish OM sources (Meyers, 2003) but C_{org}/TN_{atm} and $\delta^{15}N$ are non-conservative tracers as the original OM source signature is lost during diagenesis (Cowie and Hedges, 1994; Thornton and McManus, 1994; Graham et al., 2001). In order to investigate C budgets in mangrove ecosystems it is important to understand different OM sources and its burial in mangrove ecosystem. Anthropogenic perturbations can influence OM sources and their reactivity on short time scales and sedimentary C budgets on longer time scales (Ranjan et al., 2011). Therefore it becomes pertinent to understand C cycling in the mangrove environment. The main objectives of this study were to: (1) delineate OM sources; (2) estimate relative contribution of OM sources and burial of C_{org} in Sundarban mangrove sediments from India and Bangladesh. The study is expected to present a better understanding of the ongoing biogeochemical processes in the vertical sediment profiles. The maximum, minimum and mean values (with standard deviations) of C_{org}%, TN%, C/TN_{atm} ratio, $\delta^{13}C_{org}$‰ and $\delta^{15}N$‰ of the sediment cores I-1, I-2, I-3, B-1, B-2, B-3 and B-4 are shown in **Table 2**.

Based on the mixing model of Schultz and Calder (1976), relative proportions of terrestrial and marine organic matter in the Sundarban sediment was calculated. For the study area, the $\delta^{13}C_{org}$ values for the mangrove leaf litter (-30.22‰ in IS and -27.83‰ in BS) and benthic microalgae (-15.02‰) were used as terrestrial and marine end members. Using the above mentioned values the mixing ratio of land-derived OM or allochthonous sources (f %) and marine OM or autochthonous sources (f') was calculated using the following equation (Schultz and Calder, 1976; Minoura et al., 1997; Hu et al., 2006; Ranjan et al., 2011):

$$f\% = \frac{(\delta^{13}C_{marine} - \delta^{13}C_{org})}{(\delta^{13}C_{marine} - \delta^{13}C_{terrestrial})} \times 100 \qquad (5)$$

Further, the contribution of marine OM (f') to TOC could be estimated using the expression:

$$f' = 1 - f \qquad (6)$$

The algal-derived organic carbon (al-OC) content was obtained using the equation:

$$al - OC = TOC \times f' \qquad (7)$$

where $\delta^{13}C_{marine}$ is the marine end member value, $\delta^{13}C_{org}$ is the $\delta^{13}C_{org}$ value of sediments, $\delta^{13}C_{terrestrial}$ is the terrestrial/mangrove end member value.

Organic carbon accumulation rates (g C/m^2/y) were calculated as a product of sedimentation rate (mm/y), Bulk density (g/cm^3) and C_{org} concentration in sediments. The equation for CAR is represented as:

$$CAR = S \times BD \times \%C_{org} \qquad (8)$$

The downward depth distribution of C_{org}, TN, C_{org}/TN_{atm} atomic ratios, $\delta^{13}C_{org}$ and $\delta^{15}N$ in the sediment core present a complex set of reactions influencing the biogeochemical cycling of C and N

in the Sundarban mangrove ecosystem. It is established that the sediments from IS and BS were enriched in $\delta^{13}C_{org}$ by 4‰ to 7‰ and 3‰ to 4‰, respectively, relative to the mangrove plant matter as has been observed in other coastal environment studies (Bouillon et al., 2002, 2003; Muzuka and Shunula, 2006; Prasad and Ramanathan, 2009; Ranjan et al., 2011). The $\delta^{13}C_{org}$ ranged from -23.50‰ to -26.15‰ in IS, and -20.82‰ to -27.03‰ in BS, revealing that the OM originated from the mixture of terrestrial (higher plants) and aquatic OM. Higher relative enrichment of $\delta^{13}C_{org}$ in IS sediments

Table 2: C_{org} %, TN %, C_{org}/TN_{atm} ratio, $\delta^{13}C_{org}$ ‰, $\delta^{15}N$ ‰ in the Sundarban mangrove ecosystem

Sample ID		C_{org} (%)	TN (%)	C_{org}/TN_{atm} ratio	$\delta^{13}C_{org}$ (‰)	$\delta^{15}N$ (‰)
I-1	Min.	0.61	0.05	12.83	-24.50	1.40
	Max.	0.78	0.07	15.20	-23.56	3.33
	Mean	0.72	0.06	14.06	-23.92	2.62
	S.D.	0.04	0.004	0.66	0.27	0.57
I-2	Min	0.61	0.05	10.77	-25.69	2.38
	Max	0.83	0.09	15.54	-23.50	3.37
	Mean	0.72	0.07	12.95	-24.28	2.97
	S.D.	0.07	0.01	1.42	0.55	0.22
I-3	Min	0.58	0.05	10.83	-26.15	2.74
	Max	1.00	0.09	13.90	-23.96	3.23
	Mean	0.72	0.07	12.47	-24.60	3.04
	S.D.	0.13	0.01	0.95	0.63	0.15
B-1	Min	0.77	0.06	14.11	-27.03	1.86
	Max	1.30	0.08	23.27	-25.59	2.66
	Mean	1.00	0.07	17.04	-26.11	2.42
	S.D.	0.14	0.01	2.46	0.38	0.24
B-2	Min	0.57	0.04	13.78	-26.28	2.26
	Max	0.86	0.06	21.26	-24.59	2.91
	Mean	0.69	0.05	16.43	-25.19	2.52
	S.D.	0.08	0.003	1.61	0.41	0.19
B-3	Min	0.61	0.05	12.10	-24.98	2.31
	Max	0.92	0.07	16.67	-23.98	3.09
	Mean	0.75	0.06	14.21	-24.37	2.68
	S.D.	0.08	0.005	1.09	0.23	0.23
B-4	Min	0.51	0.04	14.78	-26.22	1.70
	Max	0.93	0.06	19.06	-24.96	2.88
	Mean	0.68	0.05	16.77	-25.58	2.21
	S.D.	0.09	0.004	1.08	0.32	0.25

may be attributed to the fact that river Bidya along which IS sediments were collected does not have freshwater flow from the upstream therefore the flow in the river is the result of storm water from the upstream and tidal pumping from the ocean which carries considerable amount of marine organic matter leading to enriched values.

Although, there was a marked presence of aquaculture ponds in IS than BS but the presence of anthropogenic activities may not significantly alter the $\delta^{13}C_{org}$ if the OM sources included aquaculture ponds and mangrove plant tissues (Bao et al., 2013). In BS, $\delta^{13}C_{org}$ showed enrichment along the terrestrial-marine gradient. OM alteration may have taken place among the sampling sites in IS and along the terrestrial-marine gradient in BS as allochthonous OM is transported along with riverine input to the ocean. Low C_{org} content with low C_{org}/TN_{atm} ratios and $\delta^{13}C_{org}$ enrichment in the sediments indicates substantial inputs of suspended matter from the mangrove creeks and adjacent bay region (Bouillon et al., 2002). The $\delta^{15}N$ values for mangrove leaves were in close agreement with the reported value in other tropical mangrove ecosystem (by Bouillon et al., 2002; Briggs et al., 2013 and references therein). The mean TN concentration in IS sediments were higher than the BS sediments whereas the $\delta^{15}N$ values were significantly depleted than the mangrove leaves for both IS and BS sediments. The higher TN content and more enriched $\delta^{15}N$ in IS than BS sediments may be attributed to $\delta^{15}N$ enriched anthropogenic pollution owing to absence of freshwater source from upstream and contribution from storm water and aquaculture ponds besides the domination of *Avicennia marina* species in the region, which may impart more TN content and enriched $\delta^{15}N$ to the mangrove sediments (Wooller et al., 2003). In BS sediments, $\delta^{15}N$ enrichment was observed along the terrestrial-marine gradient from B-1 and B-4 to B-2 and B-3 suggesting atmospheric N deposition and utilization of inorganic N depleted in $\delta^{15}N$ (Ranjan et al., 2011). In addition to this, sediment core B-2 and B-3 have more enriched $\delta^{13}C_{org}$ and $\delta^{15}N$ values which may be attributed to input of marine derived material owing to their location close to the bay (Ranjan et al., 2010). Similarly, IS sediments have more enriched $\delta^{13}C_{org}$ and $\delta^{15}N$ values than BS suggesting increased marine input in IS than BS. The C_{org}/TN_{atm} ratio of sediments ranged from 10.97-16.19 in IS and 12.10-24.02 in BS, which suggests that there is a mixed source of aquatic OM (phytoplankton and bacteria) and terrigenous OM (terrestrial higher plants/soil) (Bao et al., 2013). The results also suggest that the OM sources have dominance of phytoplankton and/or bacteria in IS as compared to BS. The downcore enrichment in the sediments may be related to the preferential removal of nitrogen (Andrews et al., 1998) as the degradation effect varied for different OM sources (marine phytoplankton vs vascular plants) (Hedges et al., 1997; Bao et al., 2013).

A simple two end member mixing model was used to assess the relative proportions of terrestrial and marine organic matter present in the Sundarban sediments (**Fig. 14**). In IS sediment core I-1, I-2 and I-3 almost 55-73% is composed of terrestrial/mangrove vegetation and 25-44% is marine derived OM. Similarly, in BS sediments B-1, B-2, B-3 and B-4 70-94% OM is composed of terrestrial/mangrove vegetation and marine OM contribute 12-30% only. This indicates that the IS sediments have more marine derived input sources than BS which has terrestrial dominance for OM sources. The marine derived input was further characterized to estimate the algal derived OC in it (**Table 3**) and it followed the same trend as followed by marine input in the region with its dominance in IS sediments than BS and increased along the terrestrial-marine gradient. The higher anthropogenic influence in the IS region may be initiating the eutrophication and enhanced production in the vicinity and thus leading to increased marine derived input in IS than BS.

The C_{org} burial rates were found to be low (<15 g $C/m^2/y$) in the present study as compared to reported values from Pichavaram mangrove ecosystem in India (Ranjan et al., 2011). CAR value showed consistent decreases with depth for sediment cores I-3 and B-3 indicating gradual decomposition of once deposited OM with depth (Purvaja and Ramesh, 2000; Alongi et al., 2005). Sediment core I-1, I-2, B-1, B-2 and B-4 do not decline with depth but are mostly linear downcore suggesting influence of variable regeneration processes that may significantly affect the C_{org} burial

rate in sediments (Gonneea et al., 2004). Low C_{org} accumulation in Sundarban points to rapid tidal export of locally produced OM to the coastal zone leading to exceptionally low CAR in the Sundarban sediments.
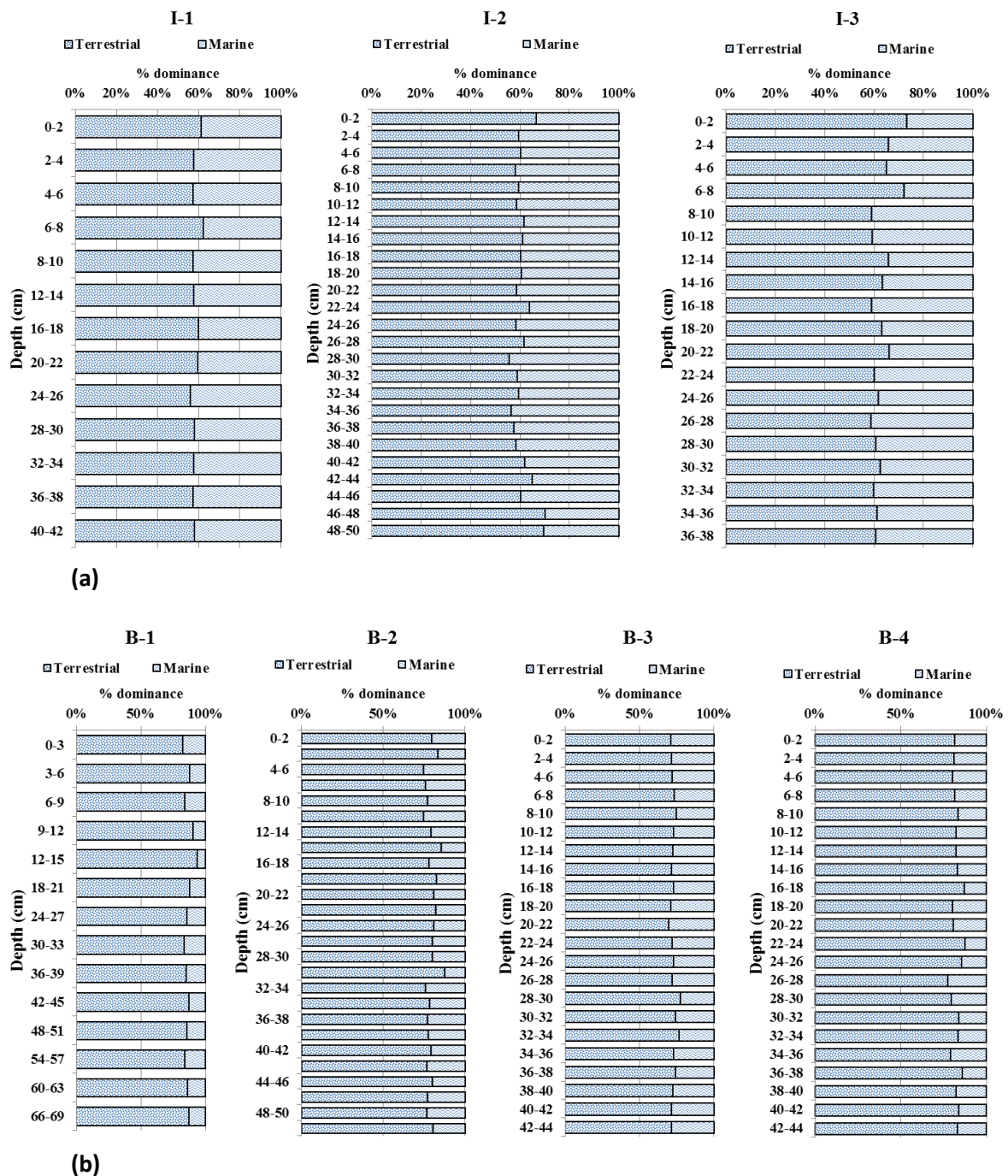

(a)

(b)

Figure 14: Terrestrial and marine organic matter contribution in (a) Indian part (b) Bangladesh part of Sundarban mangrove–estuarine complex. X-axis indicates % contribution of OM; Y-axis indicates depth (in cm)

Table 3: Percentage of algal derived marine C_{org} in the Sundarban mangrove sediments

Core	I-1	I-2	I-3		B-1		B-2	B-3	B-4
Depth (cm)	al-OC	al-OC	al-OC	Depth (cm)	al-OC	Depth (cm)	al-OC	al-OC	al-OC
2	29.72	26.53	24.21	3	15.24	2	12.70	22.35	11.70
4	31.26	33.52	34.10	6	13.73	4	10.53	22.76	13.20
6	30.95	28.51	31.23	9	17.64	6	14.26	23.00	13.65
8	27.68	33.56	25.43	12	9.63	8	16.42	22.31	9.36
10	33.10	29.47	29.49	15	5.39	10	14.81	23.05	9.62
12		29.00	27.93	18		12	15.23	19.75	10.44
14	28.99	29.25	25.46	21	9.18	14	16.70	22.02	9.65
16		31.73	29.41	24		16	12.31	21.87	12.80
18	27.52	27.42	30.82	27	14.39	18	13.13	18.59	9.37
20		27.62	25.48	30		20	12.91	17.66	13.40
22	24.53	28.74	26.72	33	15.07	22	16.41	21.52	12.06
24		29.75	24.05	36		24	10.81	21.13	9.42
26	32.19	27.89	23.78	39	13.75	26	15.89	20.72	10.03
28		30.07	23.70	42		28	14.44	20.33	14.74
30	28.93	29.31	23.82	45	14.19	30	13.43	16.80	14.31
32		26.50	21.99	48		32	8.71	16.61	10.84
34	32.04	26.51	24.11	51	14.35	34	15.53	18.86	11.56
36		26.55	24.55	54		36	14.51	18.67	14.07
38	30.63	25.75	24.36	57	14.20	38	14.44	20.10	9.78
40		28.70		60		40	14.80	19.95	11.86
42	30.24	24.66		63	17.77	42	14.51	18.08	12.74
44		24.80		66		44	15.96	17.87	15.64
46		29.59		69	12.86	46	14.67		
48		22.82				48	16.06		
50		25.20				50	14.51		
						52	12.81		

al-OC: Algal derived marine organic carbon (%)

Lignin phenols

The plant species *H. fomes*, *R. apiculata* and *A. marina* contain 9.97‰, 10.77‰ and 16.34‰, respectively, of total lignin (X_{lignin}). There is a clear spatial differences in the distribution of X_{lignin} between IS and BS sediments, IS sediments yielded high level of X_{lignin} about 6.43‰ (range: 5.34‰-6.39‰) than the BS sediments, 4.66 ‰ (2.78‰-6.78‰; Figs. 4 and 5). In IS1, X_{lignin} levels decreased from 6.34‰ to 5.34‰ in the top 15 cm and then increased to 6.56‰ at 15-40 cm (**Fig. 15**). The X_{lignin} levels increased from 6.55‰ to 7.45‰ in the top 25 cm and then decreased with the depth in IS2. In IS3, X_{lignin} levels increased from 6.39‰ to 6.19‰ in the top 20 cm and increased to 6.53‰, and then decreased with the depth (**Fig.15**). In the Bangladesh samples, no trend in X_{lignin} was observed in the top 25 cm and then increased to 6.78‰ at 40 cm (**Fig. 16**). The X_{lignin} increased in the top 15 cm in both BS2 (4.67‰-5.62‰) and BS3 (2.87‰-4.32‰). In BS4, X_{lignin} increased from 5.33‰ to 6.34‰ in the top 28 cm and then decreased with the depth (**Fig. 16**).

The *p*-coumaric acid (CAD) is the principal lignin monomer in the angiosperm leaves and yielded in very low levels from all sediment samples. The ratio of cinnamyl phenol (C) to vanillyl phenols (V) was ranged from 0.51 to 0.62 and from 0.79 to 1.25 in IS and BS sediments, respectively (Table 1).

Similarly, the ratio of syringyl phenol (S) to vanillyl phenol (V) was ranged from 0.62 to 0.72 in IS sediments and 0.62-0.82 in BS sediments. The PON/P ratio increased and decreased from surface to 35 cm in IS2 and IS3 sediments, respectively. However, in IS1 the PON/P values were slightly increased at 55 cm and then decreased. In the Bangladesh samples, the PON/P ratio decreased with the depth in BS1, BS2 and BS3 and increased in BS4. Irregular vertical pattern in the P/(S+V) ratio was observed in IS1 and IS2, whereas in IS3it decreased from 0.83 to 0.72. In BS2, the P/(S+V) ratio increased from 1.02 to 1.31 in the top 20 cm and then decreased to 1.24 at the deep. The P/(S+V) ratio decreased from 0.89 to 0.75 in BS4. In all the Indian samples, the $(Ad/Al)_V$ ratio decreased with the depth (**Fig. 15**). Similarly, the $(Ad/Al)_P$ ratio also decreased near the bottom of the core in IS1 and IS3 samples. In the Bangladesh samples, the $(Ad/Al)_V$ ratio was decreased down with the core in BS1 and BS2, and increased in BS3. In BS4, the $(Ad/Al)_V$ ratio increased from 1.23 to 1.73 in the top 32 cm and then decreased to 1.16 near the bottom of the core (**Fig. 16**). Highly variable depth pattern in the $(Ad/Al)_V$ ratio was observed in all the Bangladesh samples. The $(Ad/Al)_S$ ratio decreased from surface to the mid zone (~25 cm) in IS1 and IS2 and highly variable pattern was observed in IS3 (**Fig. 15**), whereas in the Bangladesh samples the $(Ad/Al)_S$ ratio largely decreased down with the depth of the core (**Fig. 16**).

In addition to the stable isotopes, the lignin phenols (phenolic acids, aldehydes and ketones) derived after the CuO oxidation can also be applied to trace OM sources derived from vascular plants in coastal and marine ecosystems (Dittmar and Lara, 2001; Gordon and Goñi, 2003; Prasad and Ramanathan, 2009; Loh et al., 2012). The lignin in organic matter can be accumulated in coastal and marine sediments during diagenesis because lignin is generally highly resistant to microbial degradation in the anaerobic conditions. The X_{lignin} levels the dominant mangrove species *H. fomes* (9.97‰), *R. apiculata* (10.77‰) and *A. marina* (16.34‰) indicate that that lignin was not lost during the sedimentary diagenesis in the Sundarban mangrove. Dittmar and Lara (2001) reported that lignin was removed from sediment during diagenesis in the Furo de Meio mangrove. Similar to Miltner and Emeis (2001), higher S/V ratios represent a higher abundance of angiosperms and higher C/V ratios revealing the non-woody plant contribution. Similarly, Goñi et al. (2000) also discussed that S/V and C/V ratios greater than 0.4 and 0.15 respectively infer the dominance of non-woody angiosperm tissues. The S/V ratios in IS sediments range between 0.21 and 0.72 and the C/V ratio 0.32-0.35 (**Fig. 15 and 16**) clearly indicate that OM mainly derived from the non-woody angiosperms. Similar to IS sediments, higher S/V (0.62-0.82) and C/V (0.29-0.43) ratios characterize the predominance of non-woody angiosperm in BS sediments.

In comparison to plant litter, most of the C/V ratios were very small, ≤ 0.4 (**Fig. 15 and 16**), indicate that the reactive entities of cinnamyl phenols, particularly *p*-coumaric acid, are either released or modified during the sedimentary diagenesis. However in BS sediments (BS1 and BS2), the C/V ratios are > 0.4 (Fig. 8) may be due to the selective preservation of cinnamyl phenols during the diagenesis. In general, the cinnamyl phenols are associated with lignins by ester bonds (Kirk et al., 1980) and also with carbohydrates. The diagenetic depletion of cinnamyl phenols in coastal sediments may also be influenced by either loosely associated with the lignin molecule or bound with a chemical component which is less recalcitrant than lignin (Dittmar and Lara, 2001). The PON/P ratios (IS, 0.21-0.24; BS, 0.19-0.24) are close to plant litter (0.19-0.24) representing the reactivity of *p*-hydroxyacetophenone is comparable to total *p*-hydroxyl phenols during diagenesis and microbial degradation. In this context, P/(V+S) ratio can also applied as a proxy for methylation. In aquatic ecosystems, lignin degradation usually starts with either oxidation of propyl side chain or demethylation of the methyl groups or both. But, in both IS and BS sediments, P/(V+S), $(Ad/Al)_V$, $(Ad/Al)_S$ and $(Ad/Al)_P$ ratios are lower than the plant litter explaining that aromatic ring cleavage is the dominant mechanism for the lignin degradation. The Ad/Al ratios were higher than the plant litter indicating the lignin OM degradation may be influenced by the oxidation of propyl side chain in the Sundarban mangrove ecosystem. Highly variable S/V ratios were observed in both mangrove sediments which explain that the relative diagenetic activity of syringyl phenols to vanillyl phenols

are largely regulated by in-situ redox conditions and microbial interactions with the organic matter at the particular depth. However, the relatively constant S/V ratio was observed in BS3 sediment suggesting a similar diagenetic activity for syringyl phenols to vanillyl phenols.
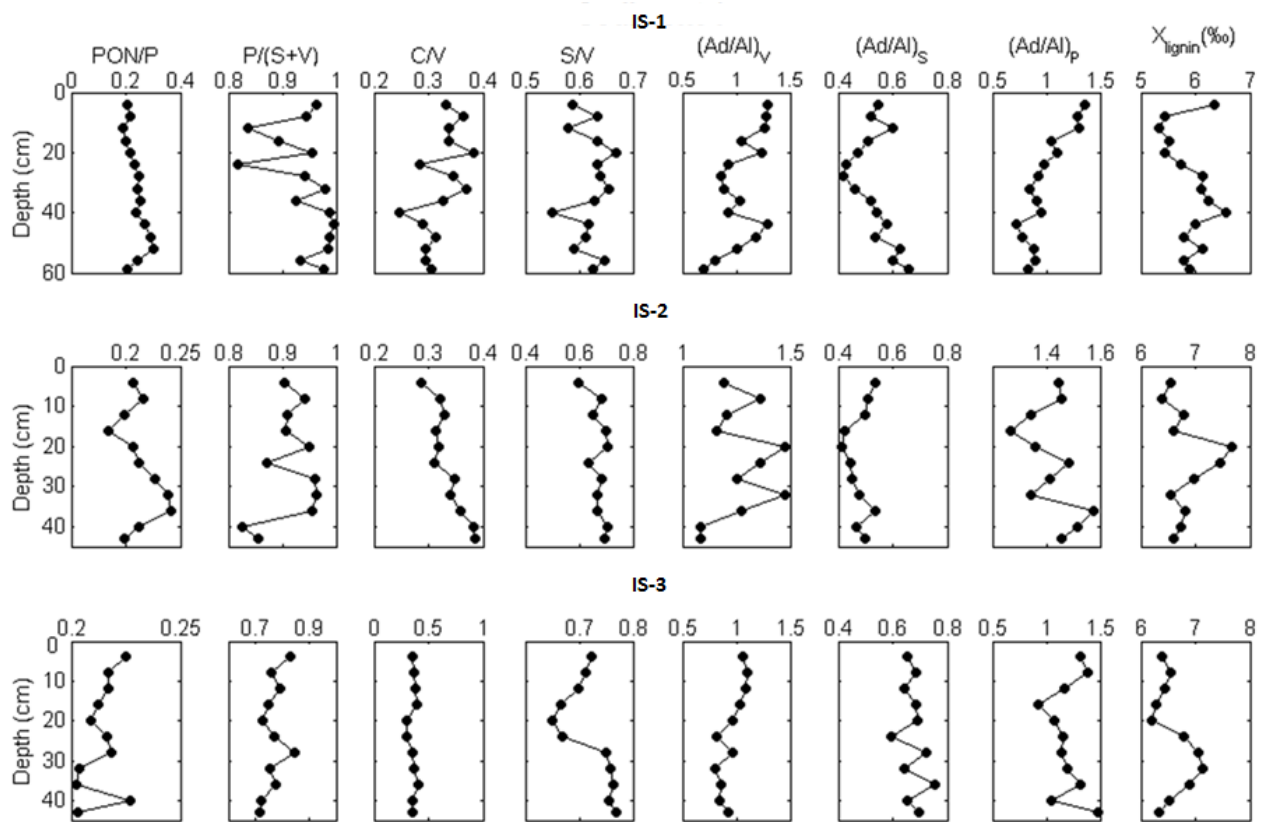

Figure 14: Vertical profiles of lignin parameters in the Indian Sundarban mangrove sediments
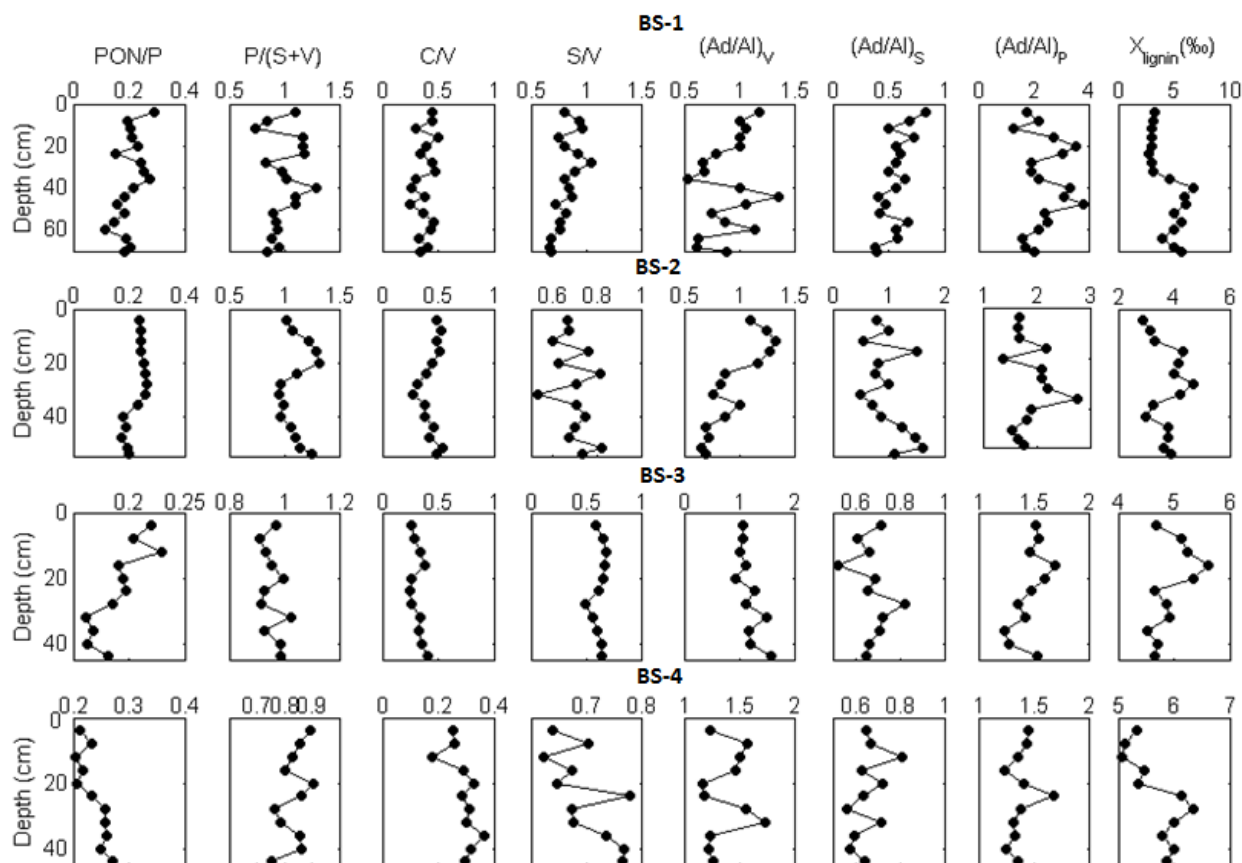
Figure 15: Vertical profiles of lignin parameters in the Bangladesh Sundarban mangrove sediments

Sedimentation rate

The ^{210}Pb activities were low (**Fig. 16**) in most of these cores. Out of the seven cores collected from the study area, only core IS-3 from the pristine mangrove forest patch provided a reliable sedimentation rate of 1 cm/yr. In all other cores (IS-1, IS-2, BS-1, BS-2, BS-3 and B-4), ^{210}Pb activities did not reach the background level and values did not decrease exponentially. In all cores except IS-3, the sediments appeared to be highly mixed.
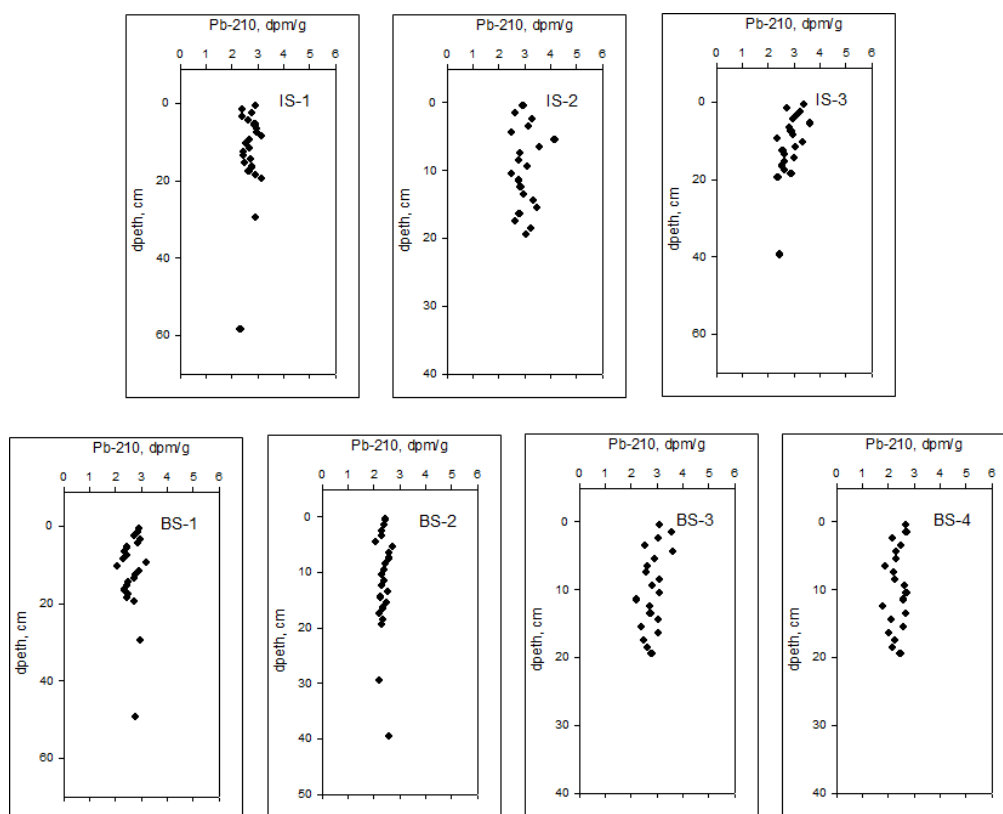
Figure 16: Activity of Pb-210 with depth in IS and BS sediments for the estimation of sedimentation rate.

4.0 Conclusions

Restate the study aims or key questions and summarize your findings

The main purpose of this study was to understand the various biogeochemical processes taking place in the Sundarban mangroves and the role of anthropogenic stress in the light of global climate change. The knowledge gained from this study will help in forming a baseline study to delineate variations in hydrological regime, climate change, human pressure and land use /and land management practices on the mangrove ecosystem dynamics which are essential components in policy making for sustainable coastal zone management. Mangroves are salt tolerant evergreen forests along sheltered estuaries, rivers and lagoons in tropical and subtropical countries. Due to their strategic location at the juncture of land and sea, they undergo regular exchange of material, playing a very crucial role in the biogeochemical cycling of nutrients and trace metals. They are considered as efficient bioreactors as they can act as sedimentary sink for trace metals, nutrients and organic carbon. However, mangroves are facing degradation due to continuous anthropogenic perturbations which may disturb the elemental cycling in the long term. The present study was undertaken in the world's largest conglomerate of mangrove vegetation, the Sundarban mangroves, in order to trace Nitrogen and Carbon biogeochemical processes in the inter-tidal mangrove ecosystem of India and Bangladesh. The study was conducted using seven sediment cores, three of which were collected in the Indian part and four in the Bangladesh part of the Sundarban. The samples were analysed for grain size analysis, trace metal concentration, Phosphorus, elemental analysis (C, N), isotopic composition of Carbon and Nitrogen and lignin and phenols to determine spatial as well as depth variations in elemental and OM cycling. Following conclusions may be drawn from the work done;

1. The Indian part of Sundarban mangroves exhibited higher trace metals concentration than Bangladesh part as confirmed by pollution indices and sediment texture has higher role to play in its distribution due to low occurrence of organic carbon.
2. Enrichment factor revealed that Sundarban sediments were least enriched w.r.t. Cd and significantly enriched in Cu, Pb and Cr.
3. Total sedimentary phosphorus in the Sundarban sediments ranged from 8.36- 11.20 µmol/g in IS; 8.80-11.40 µmol/g in BS and processes like adsorption, dissolution and precipitation play an important role in sedimentary P distribution into different phases.
4. Terrestrial and/or mangrove litter derived OM input dominates in BS sediments throughout the terrestrial-marine gradient than IS sediments which had slightly higher marine contribution.
5. Variation in δ^{13}Corg, and δ^{15}N reflects dominance of different mangrove species in IS and BS sediments.
6. Stable isotopic composition of sediments suggested that the burial of C_{org} is very low in the Sundarban mangroves indicating presence of freshly deposited OM and diluted with low Corg containing siliciclastic sediments due to high sedimentation and tidal export of autochthonous OM.
7. The lignin phenol monomers demonstrate that the Sundarban sediments did not lost high levels of total lignin (X_{lignin}) during diagenesis. The S/V ratio (IS: 0.21-0.72; BS: 0.62-0.82) and C/V ratio (IS: 0.32-0.35; BS: 0.29-0.43) indicate that OM predominantly derived from the non-woody angiosperms. Largely, the Ad/Al ratios describe the degradation of vascular OM is mainly mediated by the oxidation of propyl side chain.

5.0 Future Directions

The Sundarban mangroves are at great threat given the amount of developmental activities being planned by the two nations as a part of their economic growth. The Sundarban mangrove ecosystem is equally vulnerable to developmental pressure as it is to climate change owing to rise in sea level. With the ever increasing industrial and developmental activities the biogeochemistry of Sundarban mangrove is showing regime shifts more specifically with respect to the changes in salinity which is triggered due to low freshwater flow in the GBM basin.

Significant amount of work has been published on the biogeochemistry of mangroves which has played a crucial role in the understanding of nutrient, metal and elemental cycling. In the light of continuous advancement in analytical concepts and techniques and the natural role of mangroves as bioreactors, their continuous monitoring is imminent. Sedimentary biogeochemistry helps us in inferring the implications of human perturbations, as with increased anthropogenic influence the natural stability of the system gets disturbed which may have far reaching consequences on the short term elemental cycles and long term fluxes. The future studies are required to focus on more advanced approaches like biomarkers (e.g. lignin, phenols, tannins, fatty acids, steranes etc.),stable isotopes (e.g. δ^{34}S, δD), poly aromatic compounds, black carbon, compound specific stable isotopes etc. as this will improve our understanding of the influence of urbanization as a result of encroachment during the anthropocene.

Though mangroves are well established sinks of atmospheric carbon (in the form of above ground biomass, below ground biomass and sedimentary carbon) but their carbon storage potential is highly variable. There is a need of spatially detailed and extensive studies to be taken up in order to better predict and establish the role of Mangroves in effective mitigation of climate change. Furthermore, carrying out more studies focussing on OM preservation in the mangrove sediments will be useful in reconstructing the past mangrove environment and changes in carbon storage over time. Lack of sufficient data and continuous monitoring in the mangroves proves as a constraint to provide generalizations on a global scale.

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**Appendix**

Conferences/Symposia/Workshops
1. *12th Annual meeting Asia-Oceania Geosciences Society meeting, 2-7 August 2015, Singapore City; Pollution status of Sundarban mangroves; AL. Ramanathan, alrjnu@gmail.com, Biogeochemistry Laboratory, Lab no. 209, School of Environmental Sciences, Jawaharlal Nehru University, New Delhi-67, +91-9810689243, +91-11-26704314, +91-11-26701502.*

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List of Young Scientists
1. Dr. Alok Kumar, Research Fellow; School of Environmental Sciences, Jawaharlal Nehru University.
I was involved as Research Fellow in the project from February, 2014 till June 2015 and helped me in in attaining PhD as a part of this project. It helped me in capacity building as during undertaking this research work I had the opportunity come across considerable approaches and instruments which has only helped me in enriching my knowledge of the subject.
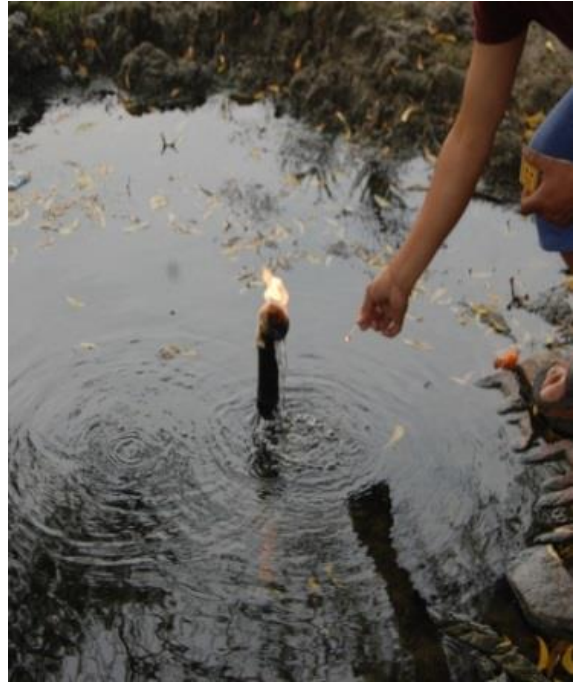
Glimpses from the Sundarban mangroves of India and Bangladesh

Project team at work