Andaman mangrove sediments: source of nutrients and sink of heavy metals

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Andaman Islands (AI) of India is a biodiversity hotspot of mangroves but biogeochemical dynamics of AI is less understood. We collected sediment samples from four AI mangrove sites and one site without mangroves for nutrients and trace metal analysis. Samples were collected from each site at the inlet of seawater (Zone A) and the other 500 m into the mangrove creek (Zone B). Nutrients (sulphate, ammonium, nitrite and nitrate) level, organic matter (OM) and carbon content were higher at Zone B of mangrove ecosystem due to the higher OM content from mangrove leaf litter decomposition and microbial degradation. Metal (Pb & Cd) content of zones with and without mangroves were similar and Igeo values indicated moderate contamination of mangrove zones of AI due to lack of anthropogenic pollution. Our results suggest mangrove ecosystems of AI are uncontaminated from heavy metals and are source of nutrients to the oligotrophic coastal ecosystems of Andaman Sea.

[Keywords: Anoxia; Metal contamination; Nutrient limitation; Oligotrophic waters; Sediment quality]

Introduction

Mangrove forests are one of the dominant and productive estuarine coastal ecosystems¹, which are biogeochemically complex and active². Mangrove ecosystem plays a significant role in the cycling of nutrients, organic matter and carbon, resulting in better functioning of the coastal ecosystems^{3,4}. Mangroves provide various ecosystem services and one of the important ecosystem services include providing refugee and acting as nurseries for commercially important juvenile⁵ fishes. On global scale, mangroves contribute >10 % of the total export of land derived dissolved organic carbon (DOC) to the coastal oceans, while covering only <0.1 % of the continental surface^{6,7}. They also help in sequestration and burial of 23 % of global organic carbon in coastal oceans⁸. Mangrove ecosystems of the estuarine zone are more dynamic and complex, resulting in export of land mediated nutrients to oceans especially in the oligotrophic waters of tropics and subtropics⁹⁻¹¹ that benefits the adjacent coastal seagrass ecosystems¹² and coral reefs^{7,11}.

Mangrove ecosystems are known for their transport of organic materials to the nearby coastal ecosystem^{7,11,13}, where mangrove leaf litter forms the base of detritus based food-web and this detritus is converted by the microbes as food source for higher trophic levels¹⁴⁻¹⁶. Along with detritus transfer mangrove ecosystem also exports dissolved ammonium, silicate and phosphorus^{7,11⁻} to the adjacent coastal ecosystem. The net export of matter from mangrove ecosystem depends on the various physico-chemical and biological processes within the mangrove sediments and water column¹¹. To export materials, mangrove ecosystems act as both source and sink of materials, directly by absorbing dissolved nutrients and carbon from terrestrial run-off¹⁷ and indirectly by absorbing them from the deposited sediments¹⁸. However, lower oxygen content of mangrove sediments¹⁹ prevents microbial degradation of matter, resulting in a transfer of undegraded organic matter to adjacent coastal ecosystem that can be utilized by other organisms in oxygen rich environment²⁰. This magnitude of transfer of materials to adjacent coastal ecosystems are dependent on the amount of fresh water input into mangrove creeks²¹. Though mangrove ecosystems are highly productive and have a rich source of organic matter, they are generally nitrogen and phosphorus deficient^{20,22,23}. To overcome this nutrient deficiency,

mangrove ecosystems depend on the efficient internal nutrient cycling of organic matter by microbial (bacteria and fungi) biomass in the sediments^{20,22,23} and mangrove leaf litter plays an important role in providing around 40 % of water soluble components for bacterial biomass⁶.

Trace metals in marine sediments are particularly of high importance due to their continuous persistence in the sediments resulting in bioaccumulation and potential toxicity to the sediment associated biota²⁴⁻²⁶. Mangrove ecosystem being at the forefront of terrestrial and marine aquatic environments acts as a trapping zone of terrestrial runoff and organic material debris. As the organic matter (leaf litter and wood) decays, it leaches out various elements. The leachate combined with land runoff also acts as a source of various pollutants that gets concentrated in the sediment; hence act as a sink for metals^{27,28}. These sediments also act as potential secondary source of trace elements that can be released back into the water column by changing environmental conditions such as temperature and pH^{29,30} and under various disturbances such as bioturbation, resuspension etc³⁰. These metals in water column and sediments become bio-available and are transferred to higher trophic levels^{27,31} exerting possible toxic effects on the associated biota through biomagnification^{32,27}. However, in mangrove ecosystems the trace metal content in water column is generally lower than sediment due to daily tidal flushing and hence low residence time³³. This increases the importance of mangrove sediments as proxies of the environmental metal contamination. Higher metal contamination due to various anthropogenic influences have been observed at different mangrove ecosystems of India, such as lead (Pb) contamination in the sediments of Pichavaram mangroves of Tamilnadu, India³⁴, while copper (Cu), manganese (Mn), nickel (Ni) and zinc (Zn) contamination was observed in the mangrove sediments of Sundarbans delta, India³³.

The coastal areas of Andaman and Nicobar Islands (ANI) are enriched with abundant mangrove forests covering 644 km^{2,35-37} of area due to favourable environmental conditions such as heavy rainfall, short dry season and high tidal fluctuations³⁸. Mangrove ecosystems of India represent 3 % of the world mangroves³⁵ and ANI represent 13 % of the total mangrove ecosystems of India^{39,35} and 50 % of the global mangrove species⁴⁰. Though these islands are enriched with mangrove forests, most of the studies on mangroves have been focused on assessment of

biodiversity⁴⁰⁻⁴², their distribution and vegetative structure^{43,41} and evaluation of mangrove ecosystem services⁴⁴. Very few studies have been carried out on the nutrient concentration of mangrove sediments of Andamans, such as nitrite, nitrate and phosphate levels in the sediments of Chidiyatappu and Rangat Bay for phytoplankton productivity estimates mangrove ecosystem⁴², whereas within nitrite. nitrate, ammonium and phosphate concentrations of mangrove sediments and water column of Aerial Bay and Chidiyatappu Bay were reported for determining water quality of mangrove ecosystems^{37,45}. Similarly, nutrients such as nitrite, nitrate, ammonium and phosphate concentration of Aerial Bay and Rangat Bay with mangroves was reported for water quality monitoring⁴⁶. Other studies have focused on the influence of anthropogenic activities on coastal ecosystem of these islands, such as influence of sewage and land run-off on the microbial biota and nutrient concentrations of Portblair Bay⁴⁷, changes in bacterial and physico-chemical properties of seawater due to land run-off⁴⁸, whereas hypoxic conditions created by sewage disposal due to human activities have been reported near mangrove ecosystem of Phoenix Jetty, South Andamans by Vishnuradhan et al.⁴⁹.

Saying that, the waters of Andaman Sea are oligotrophic⁴⁹, which requires the input of necessary nutrients from the adjacent coastal mangroves and sea grass ecosystems for better ecosystem functioning. This increases the importance of mangroves in production, cycling and transfer of nutrients to adjacent coastal ecosystems. So, the objective of our work is to quantify the various nutrient, organic matter, and carbon content of four mangrove ecosystems of Andamans and to compare the concentrations with a site without mangroves to understand the influence of mangrove ecosystem in nutrient generation and transfer. Five sites were used and from each site a zone near the seawater inlet will be compared with a zone inside the mangrove ecosystem to determine the transfer of nutrients from mangrove ecosystem. Trace metal levels were assessed to understand the metal contamination levels of these mangrove ecosystems.

Material and Methods

Study sites

The study area comprises of five different sites of Andaman Islands (AI) in Andaman Sea (Fig. 1). Andaman and Nicobar Islands (ANI) are situated in the South-east coast of Indian subcontinent in Bay of



Fig. 1 — Five study sites of Andaman Islands in Andaman Sea, India. [1] Carbyn cove (CC) [2] Chidayatapu (CH) [3] Burmanala (BU) [4] Kalapathar (KP) [5] Marina Jetty (MJ).

Bengal, Indian ocean. ANI are surrounded by Andaman Sea, harbouring a rich diversity of flora and fauna^{36,37}. Out of these five sites, four sites were situated within mangroves (Carbyn cove, Chidiyatappu, Burmanala and Kalapathar) and one site was without mangrove vegetation (Marina Jetty). All the five sites were exposed twice daily at low tides. At all the four sites within mangroves, one area was selected close to the inlet of seawater (zone A) and the second one was at 500 m upstream into the mangrove zonation (zone B). Similar zonation was used for Marina Jetty with no mangroves. Mangroves, such as *Rhizophora* species were abundant at Carbyn cove, Chidayatapu and Kalapathar, whereas Bruguiera species was abundant at Burmanala. However, at all the four sites both species were present.

Sampling

Sampling was carried out in the pre-monsoon (April-May) season of ANI. At all five sites from Zone A and Zone B, three samples were collected from 1 m apart in duplicates during low tide from a depth of 5 cm. Plastic syringes with their tips cut was used to collect sediment samples, as the syringes helped to keep the sediment intact and easy to suck up. Collected sediment samples were stored in plastic bags, stored in dark boxes and transported to laboratory for further analysis. Salinity, pH and temperature of the sediment samples were measured on field using a Salinometer (SR-028, Aichose) and Hydrolab (Hydrolab Quanta, OTT, Hydromet), respectively. In the laboratory, sediment samples were placed on big tray on white paper and air dried in room temperature. The dried samples were kept in plastic bags till further analysis.

Nutrients (sulphate, inorganic phosphate, ammonianitrogen, nitrite-nitrogen, nitrate-nitrogen, organic matter and carbon content) were analysed using UV-Visible. Spectrophotometer (Perkin Elmer, Lambda 35) using the methods described in Coastal Ocean Monitoring and Prediction System for Indian coast^{50,51}. All samples for nutrients were analysed in triplicates and quality control procedures^{50,51} were followed by careful standardization and blank measurements.

Metal analysis⁵¹

Dried sediments of one gram was taken in a flask to which 20 ml of analytical grade triacid (HNO₃: H_2SO_4 : HCLO₄: 14:1.5:4.5) was added and heated in a chamber till complete digestion of the sediment samples. Following the digestion, the samples were allowed to cooldown and were then were filtered to a 100-ml volumetric flask, distilled water was used to make the volume up to 100 ml of the filtrate. These samples were then used for the analysis of heavy metals using Atomic Absorption Spectrophotometer (AAS). For Pb the wavelength used in AAS was 283.31 nm while that for cadmium (Cd) was 280.80 nm. Distilled water was used as blanks and both samples and standards⁵¹ were analysed as triplicates.

*Geo-accumulation index*⁵²

To assess the contamination level of sediments Geo-accumulation index was used. The index of Geo-accumulation (I_{geo}) was computed using the following equation:

I
$$_{\text{geo}} = \text{LOG}_2 \text{ C}_n / 1.5 \text{ B}_n$$

where, C_n is the measured concentration of the element in the sediment, B_n is the geochemical background value derived from average shale value of the element in earth's crust⁵³ and the constant 1.5 represents natural fluctuations for the element concentration in the environment with very small

anthropogenic influence. The results obtained were compared to the below presented six classes of the geochemical index^{52,54}.

| Class | Value | Sediment Quality |
|-------|-------------------|-------------------------------------------|
| 0 | $I_{geo} < 0$ | Practically uncontaminated |
| 1 | $0 < I_{geo} < 1$ | Uncontaminated to moderately contaminated |
| 2 | $1 < I_{geo} < 2$ | Moderately contaminated |
| 3 | $2 < I_{geo} < 3$ | Moderately to heavily |
| | 0 | contaminated |
| 4 | $3 < I_{geo} < 4$ | Heavily contaminated |
| 5 | $4 < I_{geo} < 5$ | Heavily to extremely |
| | | contaminated |
| 6 | $5 < I_{geo}$ | Extremely contaminated |

Data analysis

All data was pre-checked for normality and equal variance. A two-way ANOVA using site (five sites) and location (Zone A and Zone B) as factors were used to test the significant difference (p<0.05) between variables. Data that did not show significant difference were log transformed and tested again. After ANOVA, Holm-Sidak pairwise multiple comparison was used to check the significant differences among sites and locations using SIGMAPLOT statistical software⁵⁵. All values in text are expressed as mean \pm standard error. Based on nutrients and heavy metal contents a hierarchical clustering (Bray-Curtis Similarity) was applied to describe the similarity between all five sites using PRIMER v.7 software⁵⁶.

Results

The physical parameters were similar in both, with and without mangrove sediments. The pH ranged between 7.96 ± 0.03 to 7.97 ± 0.05 among the mangrove sites, whereas at the site without mangrove

it ranged between 7.95 ± 0.03 to 7.96 ± 0.02 . Salinity was similar among all sites ranging from 31.48 ± 0.02 to 31.50 ± 0.03 . Temperature range at site with mangroves was between 30.63 to 30.66 °C, whereas at site without mangroves it ranged from 31.45 to 31.55 °C.

Nutrient concentrations of sediment at the five sites of AI were significantly different near the inlet of seawater (Zone A) and within mangrove ecosystem (Zone B). The four sites (Carbyn cove, Chidiyatappu, Burmanala and Kalapathar) with mangroves were observed with higher sulphate levels in sediment than Marina Jetty without mangroves. However, phosphate levels were higher at sites without mangrove compared to sites with mangroves (Fig. 2). The sediments at zone B of Carbyn cove (2.55 ± 0.02) $\mu g/g$) were observed with the highest sulphate levels followed by Burmanala (2.21 \pm 0.01 µg/g) and Kalapathar $(2.13 \pm 0.03 \,\mu g/g)$. Sulphate levels at zone B of Carbyn cove was 1.8-fold higher than zone A (Fig. 2a). Phosphate levels was highest at zone A of Chidayatapu (1.97 \pm 0.10 µg/g) followed by Marina Jetty (1.17 \pm 0.01 µg/g) and Kalapathar (1.01µg/g \pm 0.10), exceptions were Carbyn cove and Burmanala. Phosphate levels of Burmanala at zone B was 1.5-fold higher than zone A (Fig. 2b).

Ammonium and nitrite concentration were higher at zone B of all sites, whereas for nitrate, Kalapathar and Marina Jetty were observed with higher concentrations at zone B (Fig. 3). Ammonium concentration at zone B of Carbyn cove $(1.31 \pm 0.10 \ \mu\text{g/g})$ and Marina Jetty $(0.30 \pm 0.01 \ \mu\text{g/g})$ was 3.6-fold and 3.4-fold higher than their zone A respectively (Fig. 3a). Nitrite concentration of Carbyn cove $(0.34 \pm 0.01 \ \mu\text{g/g})$ was highest followed by Kalapathar $(0.26 \pm 0.01 \ \mu\text{g/g})$ and Marina Jetty $(0.19 \pm 0.01 \ \mu\text{g/g})$. Nitrite concentration at zone B



Fig. 2 — Sulphate (a) and phosphate (b) levels in sediments of mangrove ecosystem at five sites of Andaman Islands. Error bars represent standard errors. Significant difference between zones are indicated by different letters. Carbyn cove (CC), Chidayatapu (CH), Burmanala (BU), Kalapathar (KP) and Marina Jetty (MJ).



Fig. 3 — Ammonium (a), nitrite (b) and nitrate(c) levels in sediment of mangrove ecosystem at five sites of Andaman Islands. Error bars represent standard errors. Significant difference between zones are indicated by different letters. Carbyn cove (CC), Chidayatapu (CH), Burmanala (BU), Kalapathar (KP) and Marina Jetty (MJ).



Fig. 4 — Organic matter (a) and carbon (b) content in sediment of mangrove ecosystem at five sites of Andaman Islands. Significant difference between zones are indicated by different letters. Carbyn cove (CC), Chidayatapu (CH), Burmanala (BU), Kalapathar (KP) and Marina Jetty (MJ).

was 2.2-fold higher than zone A of Carbyn cove (Fig. 3b). Nitrate concentration was higher at Chidayatapu zone A ($0.60 \pm 0.01 \mu g/g$) followed by Burmanala ($0.32 \pm 0.01 \mu g/g$) and Kalapathar ($0.27 \pm 0.01 \mu g/g$), though the nitrate concentration of zone B of Marina Jetty was 12.4-fold higher than zone A (Fig. 3c).

Sediments within mangrove zones were observed with higher organic matter and carbon content than zones without mangroves. Among all five sites organic matter content was highest at Chidiyatappu (6.24 ± 0.20) followed by Kalapathar (5.62 ± 0.20) and Carbyn cove (5.99 ± 0.20) zone B (Fig. 4a). Carbon content was highest at zone B of Burmanala (3.80 ± 0.10) followed by Chidiyatappu (3.62 ± 0.20) and Carbyn cove (3.44 ± 0.20) (Fig. 4b). Carbyn cove and Kalapathar zone B organic matter and carbon content was 4.2-fold and 1.5-fold higher than their zone A, respectively. However, at Marina Jetty zone A was observed with higher organic matter and carbon content than Zone B (Fig. 4).

Metals (Cd and Pb) concentration were different and significant for sites with and without mangroves. Cd concentration was higher within the mangrove sediments at zone B of Carbyn cove, Chidiyatappu and Kalapathar than zone A. exception was Burmanala and Marina Jetty. However, Cd concentration at zone B of Chidiyatappu $(0.30 \pm 0.01 \text{ mg/Kg})$ was highest followed by Kalapathar $(0.27 \pm 0.01 \text{ mg/Kg})$ and Marina Jetty ($0.29 \pm 0.01 \text{ mg/Kg}$). Cd concentration of Kalapathar and Carbyn cove zone B was 1.7-fold and 1.2-fold higher than zone A, respectively, whereas Burmanala zone B was 0.6-fold lower (Fig. 5a). Pb concentration was higher at zone A of all sites, exception was Kalapathar (Fig. 5b). Highest Pb concentration were observed for zone A of Marina Jetty (1.64 \pm 0.10 mg/Kg) followed by Chidiyatappu $(1.54 \pm 0.10 \text{ mg/Kg})$ and Carbyn cove $(1.29 \pm 0.10 \text{ mg/Kg})$ mg/Kg). However, Pb concentration of Kalapathar zone B was 1.14-fold higher than zone A (Fig. 5b)

 I_{geo} values (I_{geo} <1) indicated uncontaminated to moderate contamination of sediments at all sites



Fig. 5 — Trace metals Cd (a) and Pb (b) levels in sediment of mangrove ecosystem at five sites of Andaman Islands. Error bars represent standard errors. Significant difference between zones are indicated by different letters. Carbyn cove (CC), Chidayatapu (CH), Burmanala (BU), Kalapathar (KP) and Marina Jetty (MJ).



Fig. 6 — Dendrogram for hierarchical clustering of five sites using group average linking of Bray-Curtis similarities calculated on square root transformed data. The two groups produced by threshold similarity of 90% are shown. Carbyn cove (CC), Chidayatapu (CH), Burmanala (BU), Kalapathar (KP) and Marina Jetty (MJ).

except Kalapathar zone B. Cadmium contamination was not observed at all five sites. However, within all five sites, Marina Jetty zone B was observed with higher Pb contamination followed by Chidiyatappu zone A. Overall the mangrove water outlet close to the sea were observed with higher contamination than sediments within mangrove forests (Table 1).

Dendrograms were generated based on the nutrients and trace metal levels of zone A and B at all five sites. Two groups were generated based on 90 % similarity index. The first group included zone A and B of Carbyn cove and Chidiyatappu and Burmanala zone A, whereas the second group included rest of the sites. However, zone B of Burmanala and Zone A of Kalapathar were similar with Marina Jetty zone B and A respectively (Fig. 6).

Discussion

Mangrove ecosystems act as an important source of nutrients, organic matter and heavy metals for the

| Table 1 — Igeo values of sediments for Cadmium (Cd) and lead | | | | | |
|--------------------------------------------------------------|--|--|--|--|--|
| (Pb) at all five sites of Andaman Isalnds [Carbyn cove (CC), | | | | | |
| Chidayatapu (CH), Burmanala (BU), Kalapathar (KP) and | | | | | |
| Marina Jetty (MJ)] | | | | | |

| Element | Sites | Zone A | Zone B |
|---------|-------|--------|--------|
| Cd | CC | 0.03 | 0.00 |
| | CH | 0.05 | 0.01 |
| | BU | 0.05 | 0.01 |
| | KP | 0.02 | 0.00 |
| | MJ | 0.05 | 0.01 |
| Pb | CC | 0.36 | 0.20 |
| | CH | 0.43 | 0.24 |
| | BU | 0.16 | 0.10 |
| | KP | 0.15 | 0.06 |
| | MJ | 0.46 | 0.66 |

adjacent coastal ecosystems and our results indicate coastal mangrove ecosystems of Andaman and Nicobar Islands abide to this ecosystem function with higher nutrient and lower metal concentration observed within the mangrove sediments. The physical parameters of temperature, salinity and pH observed in our site were similar to the results observed for the mangrove ecosystems in and around AI for pre-monsoon season^{37,42,45,46,57}.

The sulfate levels observed in our results within the mangrove zone B were higher, as compared to the zones without mangroves which indicates the sulfate richness of mangrove⁵⁸. The range of sulfate levels in the four-mangrove zone A were similar and zone B were 1.3 to 1.8-fold higher than sulfate levels of Portblair Bay⁵⁷ of AI. For Marina Jetty the range of sulfate (Fig. 2) were 1.2 to 1.4-fold higher than Hado Harbour of AI⁵⁷. Higher sulfate levels within mangrove sediments are result of increased sulfate reduction in the mangrove sediments sourced from decomposed organic matter³, facilitated by the sulfate reducing microbial communities found in the upper 4-6 cm of the sediment⁶⁰. However, low utilization of sulfate by the dominant microbial community and sulfate not being an essential nutrient also leads to higher levels in sediments. Lower levels of sulfate at zone A than zone B indicates about the differential production of sulfate and the exposure of these zones to wave actions, where zone A receives higher waves, tidal influx, lower resident time and drainage of tidal water compared to zone B within mangroves⁶¹.

Phosphate levels within the four-mangroves zone B (Fig. 2) in our results were higher than Chidiyatappu (1.6-fold)⁴², Sippighat (3.1-fold)⁴⁹ and Aerial Bay (4.1fold)⁴⁶ and were similar to Sundarbans mangroves sediments⁶¹. Higher phosphate levels within mangrove sediments are due to the land run-off from the nearby agricultural fields, as these mangrove areas are considered pristine in terms of anthropogenic pollution⁴⁹. Secondly, the higher organic matter input from the mangrove leaf litter and the microbial degradation, owing to rapid mobilization and recycling of nutrients during decomposition¹⁴⁻¹⁶ also leads to higher phosphate levels. Saying that, the daily tidal influx of decomposed materials to the mangrove ecosystems, their microbial decomposition and mineralization in the sediment also contributes for phosphate generation^{15,16}. Although, the mangroves of Andamans lack riverine input during pre-monsoon season, the biogeochemical phosphorous cycling effective in maintaining the global seems phosphorous range $(\langle 40 - \langle 2 \mu g/g \rangle)^{22}$ for mangrove ecosystem, as observed in our results. Lower levels of phosphate at zone B than at zone A within the mangrove ecosystem suggests the outwelling of

phosphate by daily tidal influx to the adjacent coastal ecosystem. Phosphate levels of Marina Jetty (Fig. 2) in our study were 1.6-fold and 3.6-fold higher than Phoenix Jetty ⁴⁹ and Aerial Bay^{45,46} respectively, and were similar to Rangat Bay^{42,46} which can be related to the continuous input of anthropogenic waste water discharge at Marina Jetty as there are no source of agricultural input at this site.

Ammonium and nitrate levels of Chidiyatappu zone A & B (Fig.3a & c) were 3-fold and 1.2-fold higher than previously observed for Chidiyatappu Bay^{37,42} and Aerial Bay⁴⁵ respectively, whereas ammonium levels of Burmanala zone B were 2-fold higher than previously observed values around AI^{37,45,46} and nitrate levels were 2-fold lower than Rangat Bay⁴⁶ and Sippighat mangrove ecosystem⁴⁹. Ammonium levels of Burmanala and Kalapathar zone A were similar to Aerial Bay^{45,46} and Carbyn cove was similar to Rangat Bay⁴⁶. Marina Jetty ammonium levels were 1.1-fold lower than previously recorded for Aerial Bay Jetty⁴⁵. Marine Jetty nitrate levels were 2.1-fold lower than Phoenix Jetty⁴⁹ as Phoenix Jetty receives heavy nutrient loading from anthropogenic sources of waste water discharge^{49,61}.

Nitrite levels in sediments of mangrove zone B (Fig. 3b) of our results were 4.3-fold higher than previously observed results from Chidiyatappu Bay^{37,42}, 3.4-fold than Rangat Bay, were similar with Aerial Bay^{45,46} and were 0.8-fold lower than Rangat Bay⁴⁶ of AI, whereas zone A levels were similar to these sites. Nitrite concentrations of Marine Jetty were similar to nitrite concentrations of Aerial Bay⁴⁶ and Hado Harbour⁵⁷.

Higher ammonium levels observed in the surface sediment compared to nitrite and nitrate indicates higher denitrification and anammox activity in the surface sediments of these mangrove ecosystems⁶¹. The conservation of available nitrate levels within mangrove areas due to limited riverine inputs during pre-monsoon and conversion of these nitrate into ammonium through dissimilatory nitrate reduction also adds ammonium into the surface sediment^{62,63}. However, a significant source of nitrate to produce ammonium are generally found in the sediment pore water of pristine mangrove forests like Andaman, which results in intrinsic conversion of nitrate to ammonium^{63,45}. Our study indicate, higher nitrate levels within mangrove sediment can be used to produce ammonium. Saying that, ammonium gets easily adsorbed to clay particles, which makes it

unavailable to biological uptake, thus leading to higher levels in sediments⁶⁴.

High organic matter content in mangrove sediment as observed in our study also leads to increased microbial anaerobic fermentation resulting in ammonia formation^{65,57}. On the other hand, Marina Jetty without mangroves have lower ammonium levels as the sediments are low in organic substrate (mangrove leaves) resulting in low denitrifying microbial population. The mean organic matter content of zone A and Zone B of four mangrove sites were 2 and 3-fold higher than Korampallam mangrove creek⁶⁷. Higher organic carbon in mangrove sediments is due to decomposition of mangrove leaf litter by microbial activity and hydrolysis of tannins⁵⁸ to process nutrients⁶. Secondly, these bacterial population are mostly attached to the sediments, where they naturally die and lyse to form dissolved materials²² adding organic matter to sediments. This process also prevents transfer of nutrients and dissolved organic carbon between sediment interstitial waters and water column of the mangrove ecosystem resulting in lower nutrient and organic matter content in water column¹⁵. Mangrove ecosystems are always rich in organic carbon and higher carbon content in our results was similar to the findings at mangroves of Sundarbans³³.

However, it seems that in the mangrove ecosystems of AI, much of nutrients are always stored in the mangrove generated biomass where microbial decomposition and recycling maintains the required nutrient levels. Nutrient levels in our study (premonsoon) were lower when compared to monsoon and post-monsoon levels^{37,57} indicating the land runoff due to monsoon brings heavy load of nutrients from allochthonous origin into the mangrove ecosystem of AI⁶⁶.

The concentration of Cd levels in our study for both Zone A and B were similar to Ennore creek and The Gulf of Mannar⁶⁸ south east coast of India and were 0.5-fold lower than Cd values observed for surface sediments of AI⁶⁹ and various other mangrove locations of Andamans⁶⁹, south east coast of India⁷⁰, Pichavaram Estuary⁷¹ and Tuticorin coast⁶⁷. Higher Cd concentration at mangrove zone B than zone A can be due to the use of phosphate fertilizers with Cd impurities from the nearby villages that ends up in the mangrove sediments during land run off^{72,73}. Similar higher Cd concentrations in mangrove sediments were observed at Beibu Bay in China Sea⁷⁵. However, higher Cd concentration at Marina Jetty can be due to the urban waste water discharge of Portblair city⁷⁶.

Pb concentration observed in our study were 9-fold lower than Pb levels observed for various other mangrove locations of Andamans⁶⁹, south east coast of India⁷⁰, Pichavaram Estuary⁷¹, The Gulf of Mannar⁶⁸, and Tuticorin estuary⁶⁷. Lower levels of Pb at Zone B within mangrove ecosystem can be a result of high rate of Pb accumulation in mangrove roots followed by low rate of mobilization^{27,76}. This kind of storage of Pb in mangrove roots have been observed in Rhizophora and Bruguiera species at Bhitarkanika, Odisha on the east coast of India⁷⁷ and our sites were observed with same species of mangroves. Another reason for low Pb content in our results can be due to weak correlation of Pb with organic carbon in surface sediments⁷⁸. However, the source of Pb pollution are generally anthropogenic^{75,78} and these mangrove ecosystems of AI are still considered pristine in terms of anthropogenic pollution⁶⁹. As mangrove sediments act as a sink of metals, the geochemical fraction of Pb that originates from rocks around Andamans and are incorporated into mangrove ecosystem due to land run-off and are reflected in our study.

I_{geo} values for Pb in our study were similar to sediments of south east coast of India⁷⁰ and were 2-fold lower than observed for mangrove sediments of Tamilnadu³⁴ and Korampallam creek⁶⁷, which indicates the mangrove sediments of Andamans are less contaminated from anthropogenic pollution than the mainland Indian east coast.

Similarities between the mangrove sites indicates that nutrient and trace metal dynamics of these sites were not much different due to the pristine nature of AI along with low influence of the local environmental factors such as waste water discharge and agricultural run-off^{72,73}. The similarities of Marina Jetty with Burmanala and Kalapathar indicates the influence of higher urban run-off on the nutrient and metal levels of Marina Jetty. Secondly as the samples are collected during pre-monsoon season, mangrove sites have received less land run-off⁶⁶ providing land derived DOC nutrient generation and trace metals.

Overall our study reflects the low to unpolluted conditions of Andaman Islands by heavy metals as compared to other mangroves zones of India^{69,67}. Low pollution in the mangrove locations in our study are due to lack of significant contribution from large scale industries in the AI⁶⁹. The present observed concentrations of Cd and Pb can be due to natural

factors like land run-off or erosion from local mineralogy⁷⁹ and deposition of contaminated sediments from the aftermath of 2004 Tsunami^{37,56,80}. However due to high anoxic reducing soil conditions, high decomposing activity⁸¹ and high absorptive capacity of mangrove sediments the metals bound to the sediment fractions may not be bio-available to the plants and the associated biota⁸².

Conclusion

Our results suggest that mangrove sediments of AI are source of nutrients and heavy metals which are transferred to the adjacent coastal ecosystems through daily tidal influx. Mangroves of AI take part in the generation of organic carbon and nutrients though being in the adverse tropical conditions. Though these mangrove ecosystems of AI are pristine in terms of heavy metal pollution, a constant monitoring is required to look at the effects of anthropogenic pollution. As there is lack of data for sites like Carbyn Cove, Burmanala and Kalapathar, these results can be used as an initial baseline for nutrient and metal concentration of these sites. Role of mangrove ecosystem in generation and transfer of nutrients was evident from our study. So, conservation of mangrove ecosystems around the AI should be a priority to avail the various ecosystem services provided by mangroves.

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MISHRA & MANISH: ANDAMAN MANGROVE SEDIMENTS: SOURCE OF NUTRIENTS AND SINK OF HEAVY METALS

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