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Distribution of Antimony in a Tropical Estuary Dominated by Mangroves

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ABSTRACT

Seasonal variation of antimony was studied in order to characterize its distribution in estuarine water, pore water, sediment, and digenetic behavior in the Sundarbans mangrove ecosystem. The mean concentration of dissolved inorganic Sb ranged between 230.8 *and* 303.1 *ng·L*$^{-1}$ *over the period of study with a minimum during the post-monsoon closely associated with spring diatom bloom. Molecular diffusion flux of Sb was found greater than its value advected and deposited on sediment-water interface and there was significant remobilization of Sb in the Sundarbans mangrove ecosystem.*

Keywords: *Antimony* (*III* & *V*), *Molecular Diffusion Flux*, *Phytoplankton Bloom*, *Mangrove*

1. Introduction

Antimony is ubiquitously present in the environment as a result of natural (rock weathering and soil runoff) and anthropogenic (fossil fuel combustion, mining and smelting activity and the application of super phosphate fertilizers to agricultural soil) activities [1-4]. Current world production of antimony is about 140,000 tons per year [5] and is used for several purposes such as semiconductor, diods, lead batteries, antifriction alloys, type metals, flame retardants etc. The rare element antimony has an estimated abundance of 0.2 ± 0.3 mg·kg^{-1} [6] in the earth crust and background concentrations in soils of <0.3 ± 8.4 mg·kg^{-1} [7], but it tends to concentrate in the surface soils [8]. Important anthropogenic sources of antimony in soil are vehicle emissions [9,10] and emissions of smelters [6]. Due to its versatile uses and release from this source, there is increasing concern relating to its occurrence more than admissible drinking water limit of 6 μg·L^{-1} in the aquatic system [11]. The biogeochemical process in the ocean and estuaries are complex due to the occurrence of Sb compounds in Sb (V) & Sb (III) oxidation state. The process responsible for their variation are 1) interconversion between Sb (V) & (III) oxidation state under oxic and anoxic condition 2) indiscrepency in the adsorption/desorption kinetics between Sb (III) & (V) 3) biological activity such as phytoplankton production, biovolatilisation by fungus [12-17]. These processes controlling the transformation and transport of antimony have been identified as research priorities in an ecosystem [2]. Highly productive Sundarbans mangrove ecosystem (4.71 - 6.54 Mg C·ha^{-1}·year^{-1}) with 4.85 Mg C·ha^{-1}·year^{-1} of litter production [18] and seasonal shift of phytoplankton production with diatom bloom during post monsoon period [19] could affect the antimony reactivity and cycling in the Sundarbans mangrove ecosystem situated along coastal boundary of Ganga-Brahmaputra delta. Elevated concentrations of Sb in an ecosystem could be related to anthropogenic sources and associated with high As concentration [2]. Arsenic found in the Ganga-Brahmaputra delta [20] is redistributed by biogeochemical processes in the Sundarbans mangrove ecosystem [21].

The present study was intended to identify the biogeochemical processes affecting Sb distribution and to explain its ultimate source from the Sundarban mangrove ecosystem.

2. Materials and Methods

Study area: The study site is located in the Indian Sundarban at 21˚32', 22˚40'N and 88˚05', 89˚E (**Figure 1**). This natural mangrove forest is a part of the estuarine system of the River Ganges on the northeast coast of Bay of Bengal. It covers a total area of 9630 km^2, and 4264 km^2 is comprised of intertidal zone. This area is covered

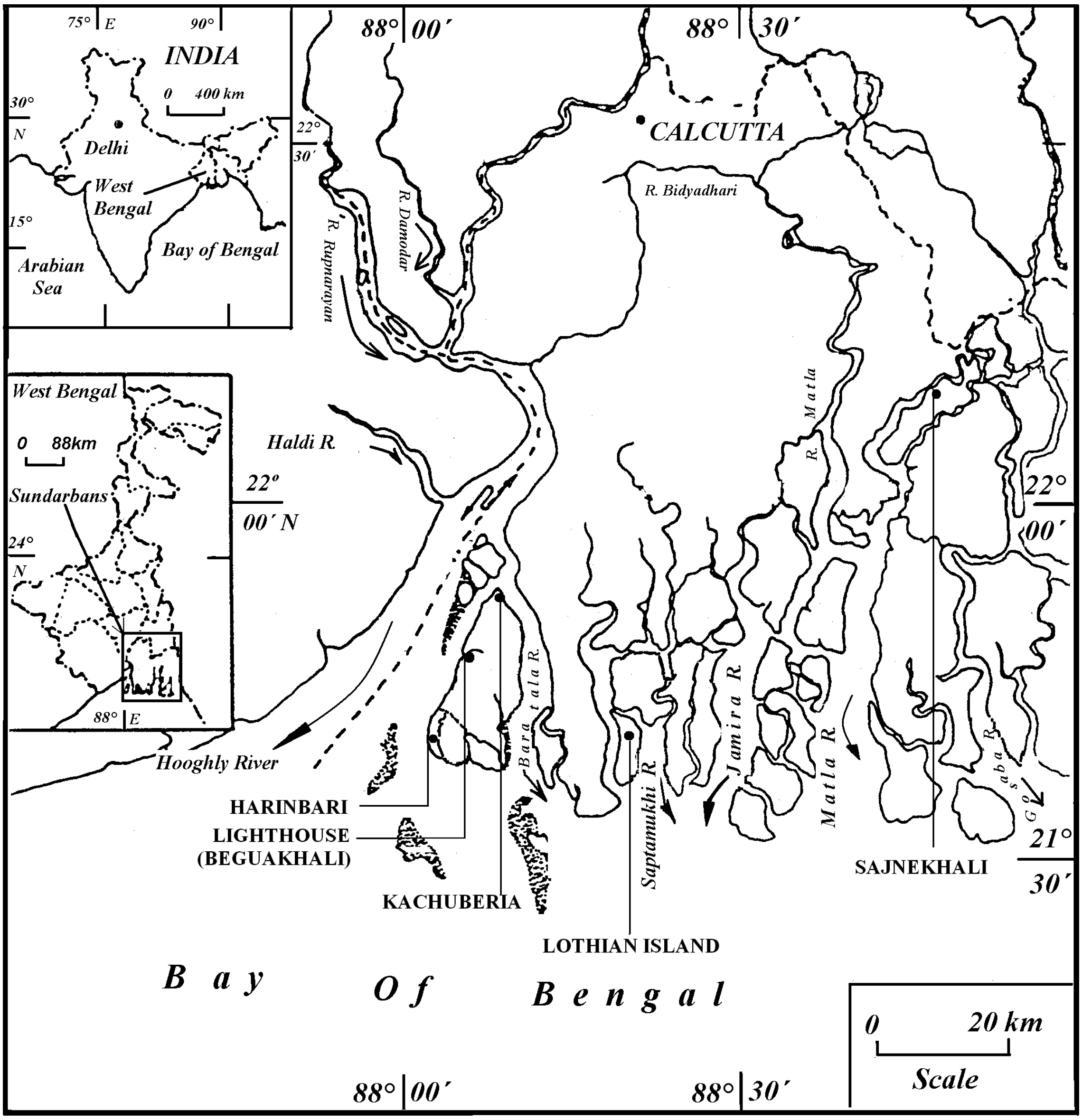

Figure 1. Map showing the station location.

with thick mangroves, which are subdivided into a forest sub-ecosystem and 1781 km^2 is an aquatic sub-ecosystem. The distance from the study area to the region, which spans from the first point in south 24 Pgs and the last point in north Malda is approximately 150 - 580 km. The Hooghly estuary, a tributary of the river Ganges, is the main artery of the Sundarban mangrove ecosystem. Farakka dam located at ~286 km upstream from the mouth of the river regulates fresh water flow through the estuary. The Ganges drains much of the southern slopes of the Himalaya and delivers an enormous supply of sediment to the Bengal fan. Suspended particulate matter (SPM) exhibited seasonality with highest level during monsoon (282.2 mg·L^{-1}) periods and lowest levels during the pre-monsoon period (12.0 mg·L^{-1}). It decreases exponentially with respect to salinity (S): SPM = 109 $e^{-0.0718} \times S$ ($r^2 = 0.5$). The annual load of sediment from the estuary to the northeast coast of Bay of Bengal was estimated to be 65.19 × 10^6 t and monsoonal runoff could account for 88% of the total transport [22]. Fresh water discharge of the Hooghly River varies between 2952 and 11,897 m^3·s^{-1} during the southwest monsoon and between 900 and 1500 m^3·s^{-1} in the non-monsoonal months. The salt front rarely penetrates beyond Diamond Harbor, which is 80 km from the mouth of the Hooghly estuary. Several discrete islands and low-lying intertidal zones are covered with thick mangrove and are inundated during spring tide. Heights of natural mangrove plants genera, such as *Avicennia*, *Acanthus*, *Aegiceras*, *Bruguiera*, and *Ceriops* >10 m are rare. The climate of the area is dominated by the southwest monsoon (June-September), northeast monsoon or post-monsoon (October-January), and pre-monsoon (February-May).

2.1. Experiments Design

Measurements were performed every month from January to December in 2007 at two sites: one located at Lothian Island in the confluence of Saptamukhi River and Bay of Bengal, and the other located at Sajnekhali, which is 117 km from Lothian Island. Samples were also collected at three stations, Beguakhali, Kachuberia, and Diamond Harbor, which covered the breadth of the salinity gradient zone. Different sites of the littoral zone covered with mangrove were selected for monthly sampling of pore water [23], sediment during low tidal expose, and tidal water during the low and high tidal phase. A corer made of stainless steel (5.5 cm i.d.) was used to extrude sediment, and sectioned at three depth intervals (0 - 2, 2 - 4, and 4 - 6 cm). Surface water samples were collected using Niskin bottles at 3 h intervals from a boat. Tidal and pore water samples were filtered (0.45 μm millipore filters, previously dried and weighed) under nitrogen atmosphere. These filter samples were stabilized by the addition of H_2SO_4 to yield a 0.1% v:v in acid-washed PP bottles, and stored in an ice box for antimony speciation analysis. Filtered tidal and pore water samples collected in PP bottles were also stored in the cold and dark without the addition of acid or $HgCl_2$ for analyses of salinity, sulfate and sulphide. Ground water collected from the tube well of ~150 m deep was preserved in an ice box after acidification for Sb analysis. Tidal and pore water samples were also collected and preserved with $HgCl_2$ for pH determination [24]. Phytoplankton was collected from surface water in the day time during high tide by using bolting silk 20 μm plankton net. For quantitative estimation, 1L samples were preserved with Lugol's solution and buffered formaldehyde. After 24hrs of sedimentation, the supernatant was reduced to a minimum volume by filtration (0.45 μm). Settled and filtered materials were combined and used for phytoplankton enumeration, identification and biovolume with the help of a Sedgwick rafter counting chamber [25].

2.2. Analytical Methods

Sulfate, sulfide, iron were analyzed by spectrophotometric method [26,27]. Relative error of accuracy was <±10%. Air-dried sediment samples were used for grain size analysis following the pipette method [28]. Freeze dried sediment sample was used for the measurement of organic carbon by the Walky-Black wet combination method [29]. Known quantity (0.5 g) of dried sediments was extracted by 0.1 N KOH solution with constant shaking for 24hrs and centrifuged and fluorescence spectra were recorded by using Perkin Elmer LS-50 luminescence spectrophotometer for the measurement of humic (HA) and fulvic (FA) acid [30]. An acid mixture (HF, HNO_3, HCl) for freeze dried sediment, suspended particulate matter samples were used for digestion in Teflon reactors to perform total antimony analysis using the Varian Hydride System-Vapor Generator (Serial No. EL0405-314) coupled to the Spectr AA 55B true Double Beam Atomic Absorption Spectrometer, following methods described elsewhere [31,32]. Measurement of dissolved Sb (III) was performed by hydride generation at pH 6 using the buffer of tris-HCl (1.9M) and 1 MHCl/1% w/v potassium iodide followed by $NaBH_4$ treatment for total antimony [33]. The analytical methods for antimony were verified before analyses of each sample batch against standard samples procured from MERCK K GaA, Germany. Relative accuracy and the coefficient of variation were 96.2% and 9.2%, respectively, for antimony.

2.3. Flux Estimate

To evaluate whether the diagenic processes could lead to significant post depositional redistribution of Sb, we estimated vertical diffusive flux. The net flux of dissolved species across the sediment-water interface (F, $ng \cdot m^{-2} \cdot d^{-1}$) is due to molecular diffusion in pore water ($-\Phi D\, dC/dZ$), and advective transport of the species in pore water (ΦUC) and on sediment particles ($\Phi UsCs$). Considering the constant ratio (K) of the distribution of chemical species in pore (C) and solid matter(Cs), and equal advection velocities of sediment particles (Us) and pore water (U), the net flux is calculated from the equation: $F = -\Phi D\, dC/dZ + \Phi\, U(K + 1)C$ [34]. For elevated concentration in pore water ($dC/dZ > 0$), the –ve value of F indicates that the net flux of antimony is directed up- ward (from sediment to water). Bulk sediment diffusion coefficient (D) was calculated from the molecular diffusion (D_0) for Sb in sea water using the equation $D = \Phi^2 D_0$ and porosity (Φ) 0.65. The concentration gradient was calculated from the Sb concentration in the overly- ing water and pore water collected from the sediment sampling interval (0 - 30 cm).

3. Results

The seasonal maximum and minimum temperatures of the atmosphere were 30.7 ± 1.5 and 21.5 ± 4.6°C in June and December, respectively. Total rainfall was recorded as 1737 and 590 mm during the SW and NE monsoon, respectively. Secchi disc transparency varied between 7 and 99 cm, and mean photic zone light energy was found to be 23.48 ± 4.5 k lux. The mean antimony concentrations varied in the tidal water from 230.8 to 303.1 $ng \cdot L^{-1}$, in pore water from 375.5 to 590.9 ng·L^{-1}, in ground water from 250.0 to 327.5 ng·L^{-1}, in sediment from 0.2188 to 0.5834 µg·g^{-1}, in suspended particulate mater from 0.08 to 0.19 µg·g^{-1}. Investigation of diurnal variations in mangrove water of antimony (Total) concentrations demonstrated an increase between low and high tide from 175.0 ng·L^{-1} to 425.0 ng·L^{-1} in October, from 128.0 ng·L^{-1} to 327.9 ng·L^{-1} in January and from 232.0 ng·L^{-1} to 464.0 ng·L^{-1} in March. Antimony concentrations in tidal water demonstrated strong seasonal variations (**Figure 2**, **Table 1**), with a maximum of 303.1 ± 91.1 ng·L^{-1} during the pre-monsoon and a minimum of 230.8 ± 102.0 ng·L^{-1} during the post-monsoon and intermediate of 279.8 ± 192.1 ng·L^{-1} during the monsoon. Antimony concentration was found to decrease in the study area after onset of the monsoon. Sb was found to be associated with particle (0.85 - 0.19 µg·g^{-1}), and was about 1.8 folds greater in the pore water than in the tidal water. Variation of Sb in the salinity gradient zone of the estuary is given in **Figure 3**, which showed increased antimony concentrations with increasing salinity. Phytoplankton population showed seasonality (**Table 1**), with the highest levels during post-monsoon periods (1.8 × 10^4 cells·L^{-1}) and lowest levels during the monsoon period (0.8 × 10^4 cells·L^{-1}). Biswas *et al.* 2010 [35] observed that the number of definable *Bacillariophyceae* species exceeded *Dinophyceae* taxa, and highest number of bloom-forming species was found during post-monsoon period.

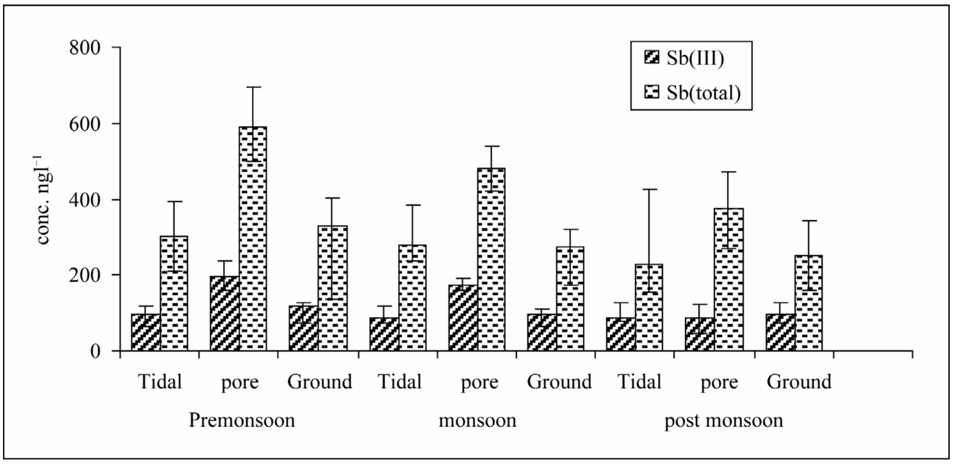

Figure 2. Seasonal variations in Sb (total) and Sb(III) for tidal, pore and ground water.

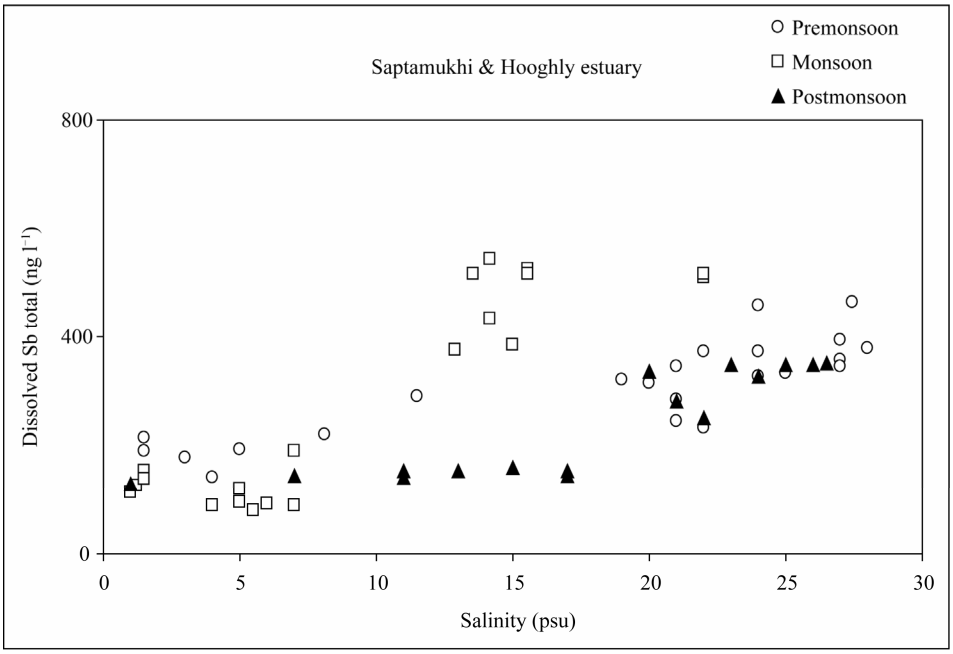

Figure 3. Salinity versus dissolved antimony (total) in the salinity gradient zone of Saptamukhi and Hooghly estuary.

Table 1. Seasonal variation of pore water and sediment quality: Salinity (S, PSU), pH, Dissolved Iron (Fe, μg·L^{-1}), Sulfate (SO_4, μM), H_2S(μg·L^{-1}), Antimony (Sb, ng·L^{-1}), Flux of Sb (F_{Sb},ng·m^{-2}·d^{-1}), Sediment texture (% of Sand, Silt, Clay), Organic C(%), HA(μg·g^{-1}), FA(μg·g^{-1}) and *Phytopankton* (*Number·L*$^{-1}$*).*

Parameters	Monsoon	Post monsoon	Pre monsoon
Pore water			
S	19.3 ± 3.7	24.3 ± 2.3	27.8 ± 0.8
pH	7.82 ± 0.22	7.79 ± 0.17	7.63 ± 0.08
Fe (μg·L^{-1})	38.42 ± 13.6	15.88 ± 13.3	29.26 ± 22.8
SO_4 (μM)	8.73 ± 1.87	11.56 ± 1.17	12.93 ± 1.79
H_2S(μg·L^{-1})	105.4 ± 28.7	169.6 ± 45.0	93.6 ± 1.4
Sb(ng·L^{-1})	480.7 ± 93.1	375.5 ± 59.9	590.9 ± 105.9
F_{Sb}(ng·m^{-2}·d^{-1})	–6.91	–4.60	–11.16
Sediment			
Sand(%)	5.83 ± 1.43	15.62 ± 4.11	5.84 ± 0.72
Silt(%)	87.5 ± 3.74	72.5 ± 5.11	79.76 ± 5.43
Clay(%)	6.16 ± 1.27	11.88 ± 3.45	14.49 ± 1.62
Organic C(%)	0.59 ± 0.05	0.66 ± 0.02	0.47 ± 0.06
HA(μg·g^{-1})	454 ± 136.8	457.8 ± 138	216.3 ± 65.2
FA(μg·g^{-1})	1298 ± 232.3	1308 ± 234.8	629.9 ± 113.1
Phytoplankton (Number·L^{-1})	**0.8×10^4**	**1.8×10^4**	**1.32×10^4**

Considering the mean distribution factor (K) of 3.36 ± 1.72 and adsorption factor (6 K + 1), the combined flux of antimony due to advection of pore water and deposition of solid particles was found to be less (4.84 to 7.61 ng·m^{-2}·d^{-1}) than that of molecular diffusion (9.44 to 18.8 ng·m^{-2}·d^{-1}). Therefore, the Sundarban mangrove ecosystem acts as a source of antimony with dispersal rate between 4.6 and 11.16 ng·m^{-2}·d^{-1}.

4. Discussion

Antimony concentrations in tidal water demonstrate strong seasonal variations with a maximum during the pre-monsoon and a minimum during the post-monsoon and intermediate during the monsoon. Concentrations of antimony in groundwater are well below the maximum contaminant level of 6 μg·L^{-1} [11]. Annual mean value for total Sb in the mangrove dominated estuaries and coastal water is 271.2 ± 235.8 ng·L^{-1}, being lower than the average values (484 ± 552 ng·L^{-1}) reported for the world estuaries and greater than the mean oceanic value (184 ± 45 ng·L^{-1}) [2]. Its greater concentration in the pore water relative to tidal water could be attributed to the possible oxidative release of organic-bound Sb from the sediment. Its non-coservative behavior with a source from the mangrove ecosystem at the lower stretch of the estuary is in conformity with the Scheldt estuary [36], Mediterranean estuary [37] However, its conservative behavior is not uncommon in a series of estuaries along the east coast of the USA, and the Rhine estuary of the Dutch Wadden Sea [38]; and mixed behavior, in other estuaries [39,40]. Considerable decrease of Sb is associated with diatom bloom in the post-monsoon. Benson and Coony [41] incubated diatom *Thalassiosira nana* with $^{125}SbCl_3$ and found protein-bound antimony, a stibnolipid, and a group of water soluble radioactive products. They suggested active uptake of Sb by diatom and its conversion into organic form. Interconversion of Sb (V) to Sb (III) followed by its excretion is a detoxifying mechanism used by *Chlorella* valgaris [42,43]. During the post monsoon, the higher ratio of Sb (III):Sb (V) (0.6:1) than the pre-monsoon (0.47:1) and monsoon (0.45:1) in the present study indicates the role of phytoplankton bloom in inter-converting oxidation state of Sb in consistent to our earlier report [20] observed for arsenic. Takayanagi and Cossa, 1997 [15] attributed the depletion of Sb and stabilization of Sb (III) in the surface of Lake Pavin, France to the uptake by phytoplankton. Non conservative behavior of Sb owing to biological uptake of Sb by phytoplankton is a slow process relative to the scavenging rate by aluminium in the estuarine water [44]. Stepwise multiple regression analysis demonstrates that sulphate, H_2S and iron comprise 60% of the variability of total antimony in pore water.

Total Sb (ng·L^{-1}) = 1318 - 5.38 S – 60 pH + 284 SO_4 – 1.81 H_2S + 0.84 Fe -723 Org-C (R^2 = 84.5%, F=4.56, n = 12, p = 0.059). Out of the six factors p is found relatively more significant for organic carbon (p = 0.059), sulphate (p = 0.084) and iron (p = 0.064). Antimony could be present in the soils as slightly soluble sulphide and could remain in association with arseno pyrite [45,46]. Oxidative release of antimony from both pyrite and soil organic carbon could explain its elevated concentration in pore water. Deng *et al.*, [47] and Chen *et al.*, [48] found from the analyses of lake and pore waters that the major part of Sb was associated with natural organic compounds (up to 85% of total Sb) and the rest was in inorganic Sb (V) and Sb (III) forms. Few recent experimental studies reported association of Sb with aqueous humic acids and demonstrated moderate binding of Sb (III) with humic compounds [49,50]. However, the identity of binding sites, stoichiometry and structure of complexes remained uncertain. This is due to the fact that natural organic matter (dominated by humic and fulvic acids) is present in extremely complex poly-functional structure, which precludes assessing unambiguously sorption mechanisms or nature of aqueous complexes and identifying chemical sites (potentially numerous) responsible for Sb binding.

Sediment-water molecular diffusive flux of antimony is greater than the combined flux due to advection of pore water and deposition of solid particles over the sediment and the Sundarban mangrove ecosystem acts as a source for antimony with significant diagenetic remobilization.

5. Acknowledgements

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