International Research Journal of Environment Sciences ISSN 2319–1414
Vol. **2(3),** 62-66, March **(2013)** *Int. Res. J. Environment Sci.*

Review Paper

Geochemical Assessment of Heavy Metal Contamination in Mangrove Ecosystem: A Brief Overview

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Available online at: www.isca.in
Received 7th January 2013, revised 2nd February 2013, accepted 3rd February 2013

Abstract

Heavy metal contamination in the mangrove ecosystems is the matter of concern as its long persistence and continuous anthropogenic inputs. Depositional environment also affects the concentration of heavy metals as its significant positive correlation with organic carbon content and particle size of the sediments. Heavy metal concentrations is higher in the upper layer of mangrove sediments as compares to mud flats as the higher content of fine particle and organic matter in the upper sediment layers of the mangrove sites. Heavy metals concentration depends upon the factors influencing its content in the sediments as well as on release.

Keywords: Mangroves, ecosystem, sediment, heavy metals, organic matter.

Introduction

A significant amount of the intertidal flats in the estuary is contaminated with heavy metals due to industrial and urban development. Sediments and their associated organic matter are expected to be major sinks for metals[1]. Metal concentration in the sediments is determined by the input from various sources and the extent to which the sediment is capable to bind and release. Soil and sediment characteristics such as pH, cation exchange capacity, organic matter content, redox conditions, chloride content and salinity determine metal sorption and precipitation processes, which are also related to the metal mobility, bioavailability and potential toxicity[2]. Depositional environments influence the sediment characteristics as the higher organic matter and clay contents and sulphidecontents enhance metal accumulation in the intertidal sediments, whereas higher salinities resulted in reduced metal accumulation[1,3]. Salinity effects are not confined to the complexation capacity of salt anions but it also affects mobility of metals. When Ca^{2+} and Mg^{2+} are abundant in the soil solution, metals will also be mobilized from soil particles as a result of competition between these divalent cations and the metal ions[4]. Consequently, heavy metals pose a potential threat to various terrestrial and aquatic organisms[5].

Mangrove forest is considered to be one among the highly vulnerable ecosystems of the world and continuous anthropogenic activities ranging from deforestation to pollution threaten the survival of mangrove habitats throughout Asia[6, 7]. However, a limited scientific data on the toxic levels of heavy metals found in themangrove forest plants in India, which is experiencing economic boom and industrial outburst in recent decades.

Factors affecting heavy metals content in the sediment

Factors influencing heavy metal accumulation: Characteristics of the sediments: Heavy metal in sediments comes from natural (rock weathering, soil erosion, and the dissolution of salts) as well as anthropogenic source[8]. The organic matter content in the sediments lead to relatively higher concentrations of heavy metals accumulation[9]. Sediment grain size significantly influences the concentration of heavy metal in estuarine sediments as theclays fractions attributed to high specific surface area, favour adsorption processes[10]. Incidentally, in the estuarine environment more silt and clay composition has been recorded, which leads to higher concentrations of heavy metals[11]. It has also reported that coatings of organic matter prevalent in finegrained sediments bind a variety of trace elements[12].

Depositional environments: The speciation distribution of heavy metals is ranked asin the order of residual > bound to Fe–Mn oxides > bound tocarbonates > bound to sulfides and organics > exchangeable[13] (figure 1). Due to large specific surface area andhigh superficial charge density of Fe–Mn oxides andHydroxides, this causes strong chemical adsorption[14]. Fe and Mn may act as oxidant or reductant in naturalenvironment. Fe–Mn oxides or hydroxides are considered as substantial scavengers of trace elements. A rapid decrease in the concentrations of Fe and Mn from surface to certain depth suggesting diagenetic enrichment[15] during which Fe-Mnoxyhydroxides dissolve in the partly reduced sediment layer producing Fe^{2+} and Mn^{2+} species, which migrate upward in the sediment column and get precipitated near the oxic-suboxicinterface. Cd and Mn tend to associate with carbonates and settle down from water column. Cd is also reported to get bounded with sulfides and organics. The speciation distribution of Cu is complex in the sediments. Non-residual Pb is also abundant in the surficial sediments[13]. In the estuary, high porosity of the sediment due to available sand favors oxygenation and re-mineralization of organic carbon. In such conditions, the precipitated Fe oxyhydroxides are not converted to pyrite[16]. The elevated metal contents in the estuary and an increase in the number of elements associated with Fe suggest that co-precipitation of iron hydroxide along with scavenging of other elements could be the probable mechanism as well as intense chemical weathering of the estuarine environments behind the accumulation of metals in the estuary[17]. Land-based anthropogenic factors (mining, fertilizers, pesticides and paint industries) are the main source of Cd pollution[18].

Factors influencing heavy metal release

Salinity: Concentrations of heavy metals (Pb, Cu, Zn) in the water column gradually decreased from mainland to coastal area, but Cd behaved in an opposite way. The reason of the trend may rest with the gradually increasing salinity. Along mainland tocoastal area, heavy metals in the sediment were susceptible to the variety of salinity and could befrequently shifted at the water sediment interface[19].

Cl^- : Cd could exist by formation of complexes with chlorine in the sea. The release of Cd from sediments could be accelerated by abundance of Cl^- ion. Very few investigations have been done on the relationship between amount of Cd released from sediments and $C1^-$ content in the water. Still, there is nofirm explanation about theimpact of Cl^- ion on the release of other heavy metals such as Zn, Cu and Pb[20].

SO_4^{2-} : Sulfate ions are major anions in seawater. In general, heavy metal concentrations in the water increased to a certain extent as the SO_4^{-2}increasing[8].

HCO_3^- : Heavy metals accumulated in marine sediments are prone to form soluble complexes with HCO_3^-, which leads to the release of the heavy metals from the sediments. Heavy metals tend to form insoluble carbonate salts where the dominating species is CO_3^-. This process could wipe off the heavy metals from the seawater to reduce the pollution of the seawater to some extent[8].

Effects of mangroves reforestation

Physico-chemical properties: The mangrove reforestation increases fine particle and organic matter content in the upper sediment layers[21]. The baffle effect of mangrove roots and trunks may be the cause of increase in fine particle content by enhancing fine particle settling and stabilization[22]. The increase in organic matter content may be derived from decomposition of root material and leaf litter. The mangrove roots can diffuse oxygen into the rhizosp here, increasing redox potential in the sediment, particularly in the upper sediment layers, where root density is higher[23]. Mangrove reforestation results in rapid acidification of sediments leads to a significant decrease in pH. This phenomenon may be caused by the microbial decomposition of mangrove litter and oxidation of FeS_2 and FeS[24].

Heavy metal accumulation: The concentrations of Pb, Zn, Cu, Cr and Ni in the upper layers of mangrove sediments are greater as compared to the upper layer sediments of mud flats, shows the accumulation of heavy metals as a result of reforestation. This accumulation may be explained by the increase in fine particle and organic matter content in the upper sediment layers of the mangrove sites[25,26] (figure 2(a-d)). However, similar correlations are not found at the mud flat site. This may be attributed to frequent sedimentre-suspension, which strongly disturbs the spatial distribution of heavy metals in sediments. Fluctuations in metal concentrations at certain depths may result from leaching, post-depositional remobilization and bioturbation[27].There are no significant correlations among most of these heavy metals, indicating they have different anthropogenic and natural sources (table 1). The chemical adsorption of metals, rather than physical or deposition of these metals with organic matter on the top of surface sediments by means of a stable metal ions-ligands association (through the functional groups such as –OH, $–NH_2$, −COOH of the organic matters) leads to significant correlation between organic matter and metals in the sediment[28].

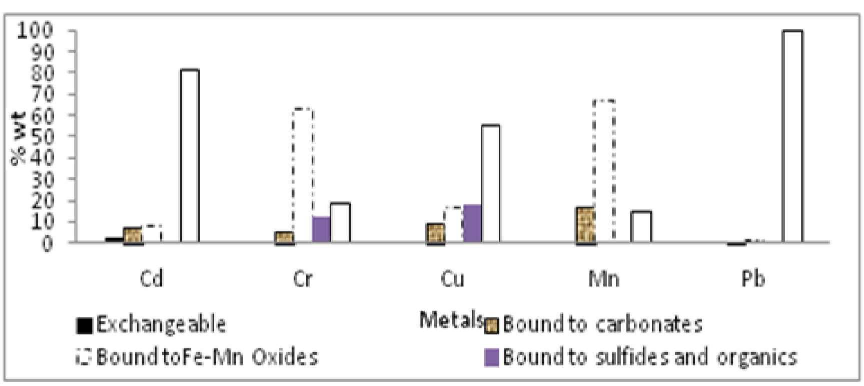

Figure-1
Heavy metals speciation[13]

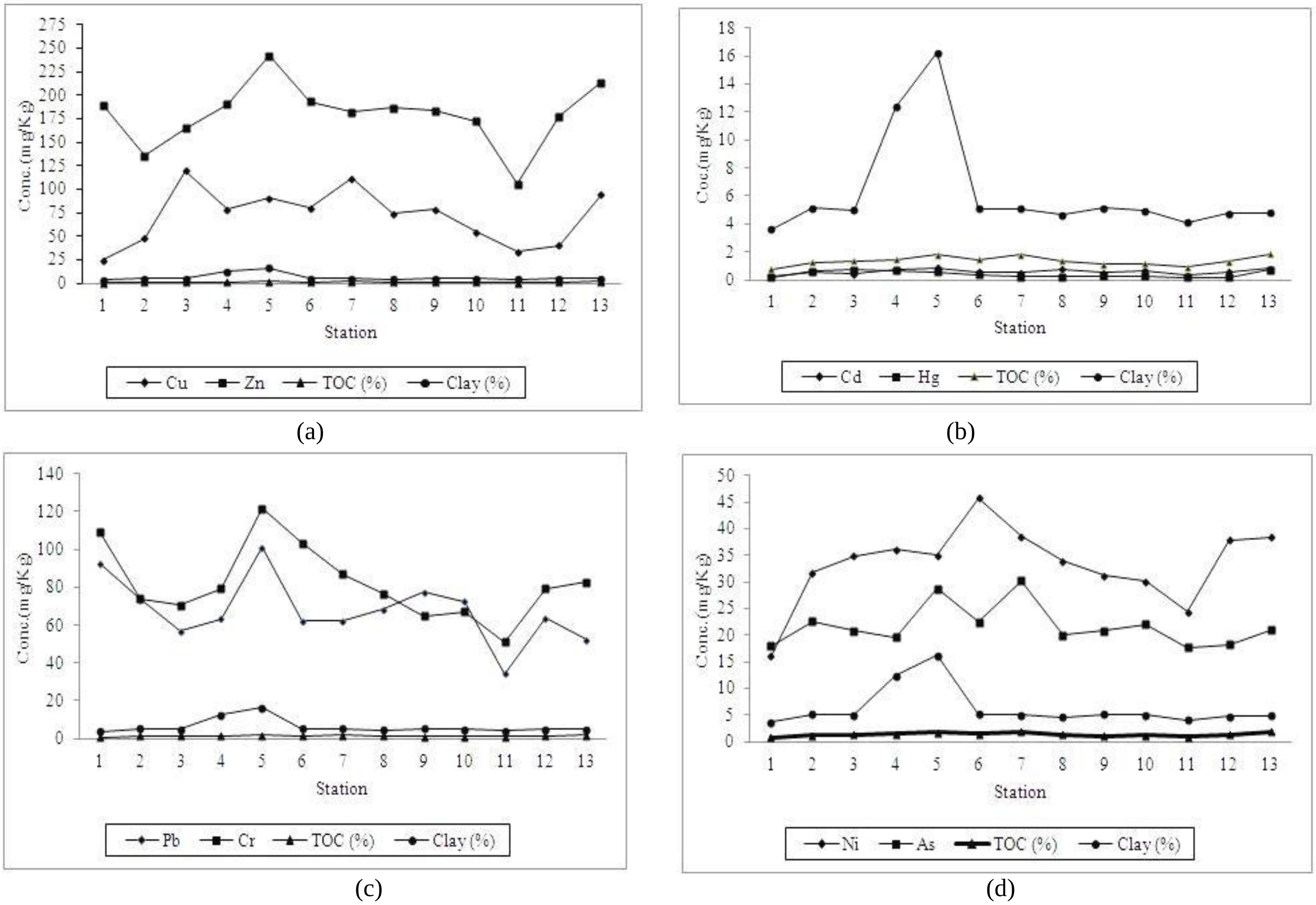

Figure-2
Total organic carbon (TOC) and clay content in the sediment vis-à-vis metal concentrations in the surface sediment[26].

Table-1
Correlation of heavy metals accumulation with particle size and organic matter content in the sediment[26]

	Cu	Zn	Pb	Cd	Cr	Ni	Hg	As	TOC (%)	Clay (%)
Cu	1									
Zn	0.44	1.00								
Pb	-0.08	**0.60**	1.00							
Cd	0.38	**0.65**	0.22	1.00						
Cr	0.12	**0.76**	**0.70**	0.26	1.00					
Ni	**0.64**	0.36	-0.23	**0.56**	0.13	1.00				
Hg	**0.52**	0.27	0.00	0.46	0.11	0.36	1.00			
As	**0.59**	0.43	0.34	0.38	0.44	0.41	0.17	1.00		
TOC (%)	**0.76**	**0.59**	-0.02	**0.73**	0.34	**0.79**	**0.51**	**0.70**	1.00	
Clay (%)	0.28	**0.56**	0.46	**0.59**	0.48	0.21	0.46	0.44	0.46	1.00

Comparative discussion: Heavy metals in the mangrove sediments have been reported by several authors, which have made some insight about the heavy metal contamination (table 2). Some of the naturally occurring elements such as Cu, Mn, Fe, and Zn are essential micronutrients for plants, but can become toxic at concentrations higher concentration[29]. Heavy metal cycling is a serious problem reported in mangroveecosystems[25]. In the mangrove ecosystems heavy metals show significant positive correlation with silt and clay due to high silt and clay contents provide surface for adsorption of the metals[18]. Relatively higher concentration of Fe in the mangrove ecosystems highlights the possibility of precipitation of Fe asiron sulfides[30]. A significant correlation has been observed between organic matter and metal content in the sediment as the fine grained sediments is coated with organic matters, which influence the binding of a variety of metals[12].

Table-2
Comparative representation of heavy metals concentration (mg/Kg, except some report related to Fe) of estuarine sediments

Location	Fe	Mn	Cu	Cd	Co	Cr	Ni	Pb	Zn	Reference
Pichavaram, India	24998	801	132.3	34.74	–	617	252.1	143.8	106	Ranjan et al. 2008
Gulf of Mannar, India	1.26 (%)	305	57	0.16	15	177	24	16	73	Jonathan et al. 2009
South East Coast, India	2.72 (%)	373	506.2	6.58	8.10	194.83	38.61	32.36	126.8	Raj and Jayaprakash, 2007
Pichavaram, India	32482	701	32	6.96	–	141.2	62	11.2	89	Ramanathan et al. 1999

Conclusion

The source of heavy metal contamination in the sediment may be the natural and anthropogenic. Heavy metal concentration in the sediment depends upon the factors influencing its accumulation and release. Factors like depositional environment, particle size of the sediment and organic matter content play a vital role in accumulation of metal contaminants. However, factors like Salinity, Cl^- , SO_4^{2-}, HCO_3^- influences its release. Mangroves reforestation increases fine particle and organic matter content in the upper sediment layer and hence heavy metal accumulation. Depth-wise fluctuations in metal concentrations may result from leaching, post-depositional remobilization and bioturbation. A very few research work have been carried out to assess the contamination of heavy metals in the mangrove ecosystems. Current review paper is providing the insight about the geochemical processes; a complex mechanism may operate in the system, which needs further research.

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