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Kinetic speciation and bioavailability of copper and nickel in mangrove sediments

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ABSTRACT

An attempt was made to establish a mechanistic linkage between chemical speciation of copper and nickel, and their bioavailability in mangrove ecosystem. Kinetic speciation study was performed to determine the concentrations of labile metal-complexes and their dissociation rate constants in mangrove sediments. Concentrations of copper and nickel in the mangrove roots were used as indicators of their bioavailability. It was found that the bioaccumulation of both the metals gradually increased with the increasing concentrations of the labile metal complexes and their dissociation rate constants in the mangrove sediments. This study shows that concentration of labile metal (copper and nickel) complexes and their dissociation rate constants in mangrove sediment can be a good indicator of their bioavailability.

1. Introduction

Mangroves act as natural buffers between the land and sea. Mangrove sediments serve as natural sinks and play an important role in controlling trace/heavy metal distribution, speciation and their bioavailability in coastal environments. Complexations of metal (trace/heavy) with different binding phases in mangrove sediments regulate transport, bioavailability, and toxicity of metals in the system. Importance of metals speciation and their bioavailability in mangrove sediments are recognized but poorly understood.

Various experimental methods/techniques are being used to determine speciation (and dynamic/labile complexes) of metals in soils and sediments. The approaches include batch techniques (Beauchemin et al., 2002; Bermond and Varrault, 2004; Yu and Klarup, 1994), flow techniques (Beauchemin et al., 2002; Shiowatana et al., 1999; Silva et al., 2007), kinetic extraction methods (Chakraborty and Chakrabarti, 2006; Chakraborty et al., 2012a, 2012b, 2013, 2011, 2009), Diffusive Gradients in Thin Films technique (Bermond et al., 1998; Fangueiro et al., 2002; Town et al., 2009). However, the kinetic extraction method has been found to be a simple and sensitive technique (Chakraborty and Chakrabarti, 2006; Chakraborty, 2012).

This time dependent metal extraction study from sediments has been reported to be useful to ascertain the potential availability and mobility of metal and its migration in a polluted or naturally contaminated soils/sediments (Beauchemin et al., 2002; Bermond and Varrault, 2004; Fangueiro et al., 2002). This method is capable of determining kinetically distinguishable (labile and inert) metal complexes (in soil/sediment) and their corresponding dissociation rate constants in a system.

Labile metal complexes (with fast dissociation rate constants) can therefore be used to estimate bioavailability of metal if a kinetic model can be constructed to represent the process of biological uptake. In this study, an attempt was made to establish a mechanistic linkage between copper and nickel speciation, and their bioavailability in mangrove ecosystem. Concentrations of accumulated metals in mangrove roots have been reported to be a good indicator of bioavailability of metals in the same system and this observation was related to our values for speciation as a test of bioavailability. The objective of this study was to prove the hypothesis that labile metal complexes from mangrove sediments contribute to the bioavailable metal flux and increase its bioaccumulation in the mangrove roots. This is the first attempt to establish a linkage between metal (copper and nickel) speciation, and their bioavailability in a mangrove ecosystem.

2. Materials and methods

2.1. Study area

Sediment samples were collected from mangrove forests located at Divar Island in Goa, west coast of India. The adjoining Mandovi estuary was used for transportation of iron ore from

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mines located upstream. Sediments were collected from five environmentally relevant sampling sites (Fig. 1) at Divar Island, during low tide, in December 2013. Undisturbed sediment cores were collected by using PVC cores (inner diameter 7.5 cm, 20 cm length).

2.2. Textural analysis of mangrove sediments

Textural analysis of the sediment was done by (after sieving with 63 μm sieve size) laser size particle analyzer (LPSA.). Malvern Mastersizer 2000 was used for size particle analysis. The detailed procedure has been described in the literature by Ramaswamy and Rao (2006). The data are presented as weight percentage (wt%) in this study.

2.3. Elemental analysis

Bulk sediment samples were analyzed for total carbon (TC), total inorganic carbon (TIC), total nitrogen (TN) content. TC and TN in sediments were determined using Flash 2000 CHN-elemental analyzer (Thermo Fisher Scientific Incorporation). Precision of the analysis was within ±5%. Soil NC was used as certified reference material. TIC was determined by coulometry (UIC coulometrics). Anhydrous calcium carbonate was used as standard material. Relative standard deviation of the analysis was within ±2%. Total organic carbon (TOC) was derived from deducting TIC from TC.

2.4. Determination of metals (Cu, Ni, Fe, Mn) in the sediments and mangrove roots

Multiple sediment sampling was done at each station. The composite sediments were stored at −20 °C, and then freeze dried (Esquire Biotech Pvt. Ltd Model-SK 50L, Chennai, India). The dried composite sediment samples (from each station) were homogenized and ground-milled; the sediment samples were subsequently stored at 4 °C until needed. Multiple fine nutritive mangrove roots (sp. *Avicennia officinalis*) were collected from the sampling station. The surfaces of the mangrove roots were thoroughly washed with ultrapure water for complete removal of sediments from the roots. All the roots were freeze dried until constant weight obtained. The dried roots were ground-milled and homogenized. The total metals concentrations in the mangrove roots were determined by digesting 0.1 g of ground-milled and homogenized roots samples with 10.0 cm^3 of acid mixtures of HF, HNO_3 and $HClO_4$ (in 7:3:1 ratio) on hot plate at 200 °C. The samples were digested and evaporated to dryness. The residues were re-dissolved in 2% HNO_3 and analyzed by graphite furnace atomic absorption spectrometer (GFAAS). Total concentrations of Cu, Ni, Fe, and Mn were determined in the studied sediments.

2.5. Kinetic extraction procedure

Two grams (2.0 gm) of sediment was added to 200 cm^3 of 0.05 M EDTA solution (at pH 6.0) (Merck Pvt. Ltd.) in a Teflon

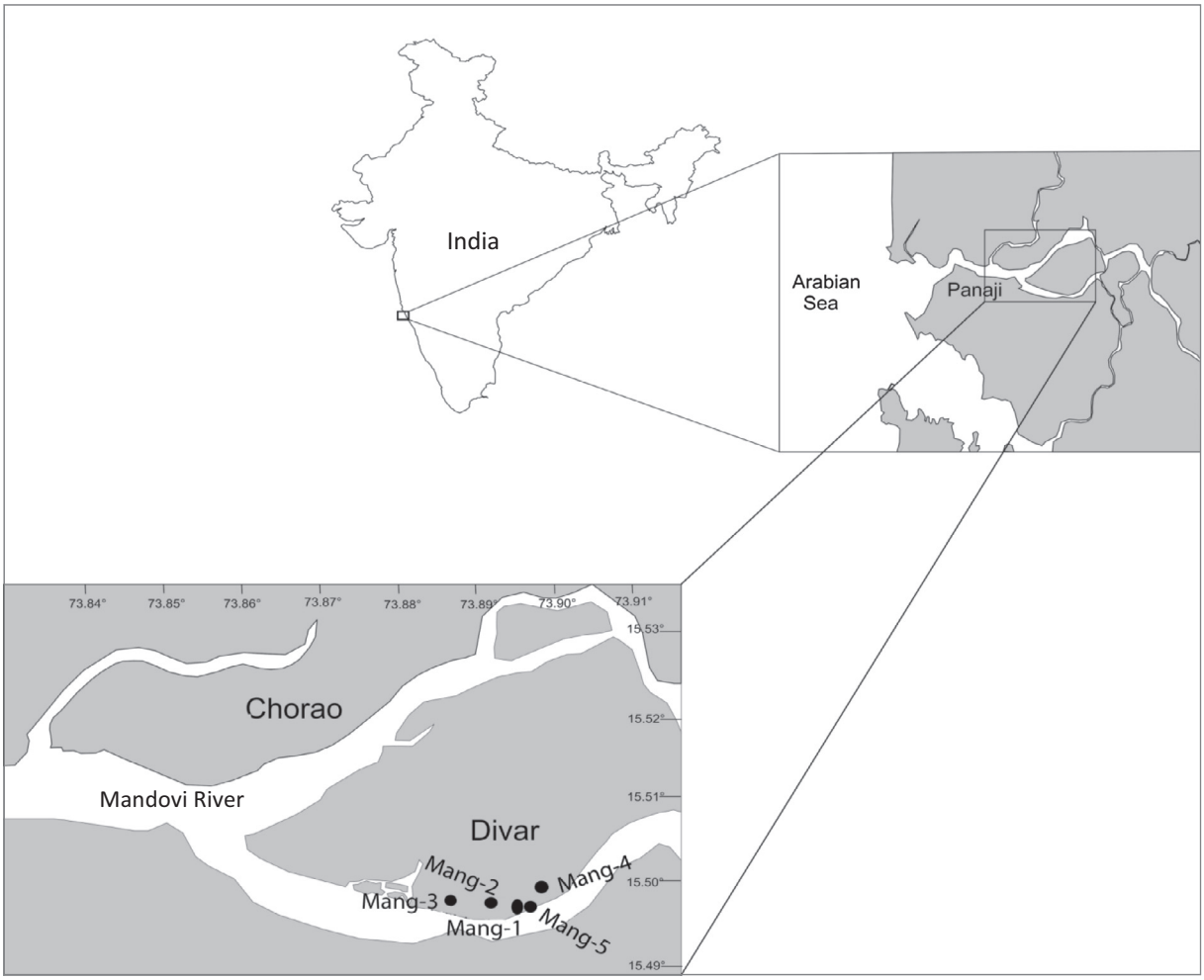

Fig. 1. Map of the sampling areas in the mangrove areas located in Divar Island (west coast of India). The filled circles are the locations of the five sampling sites.