Science of the Total Environment 463–464 (2013) 667–674

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Trace metal biogeochemistry in mangrove ecosystems: A comparative assessment of acidified (by acid sulfate soils) and non-acidified sites

Bibhash Nath [a,*], Gavin Birch [a], Punarbasu Chaudhuri [a,b]

[a] School of Geosciences, University of Sydney, Sydney, NSW 2006, Australia
[b] Department of Environmental Science, University of Calcutta, Kolkata 700 019, West Bengal, India

HIGHLIGHTS

- Role of wetland acidification on trace metal distribution in mangrove soils and tissues was studied.
- Trace metal concentrations in soils of affected and control sites were not significantly different.
- Fe and Ni accumulated in significant amount in mangrove tissues of affected sites.
- Mn, Cu, Pb and Zn accumulated in significant amount in mangrove tissues of control sites.
- Differences in trace metal accumulations in mangrove tissues suggest geochemical control.

ARTICLE INFO

Article history:
Received 17 January 2013
Received in revised form 5 June 2013
Accepted 5 June 2013
Available online 8 July 2013

Editor: Charlotte Poschenrieder

Keywords:
Trace metals
Acid sulfate soils
Gray mangrove-*Avicennia marina*
Bio-availability
Bio-accumulation

ABSTRACT

The generation of acidity and subsequent mobilization of toxic metals induced by acid sulfate soils (ASSs) are known to cause severe environmental damage to many coastal wetlands and estuaries of Australia and worldwide. Mangrove ecosystems serve to protect coastal environments, but are increasingly threatened from such ASS-induced acidification due to variable hydrological conditions (i.e., inundation–desiccation cycles). However, the impact of such behaviors on trace metal distribution, bio-availability and accumulation in mangrove tissues, i.e., leaves and pneumatophores, are largely unknown. In this study, we examined how ASS-induced acidifications controlled trace metal distribution and bio-availability in gray mangrove (*Avicennia marina*) soils and in tissues in the Kooragang wetland, New South Wales, Australia. We collected mangrove soils, leaves and pneumatophores from a part of the wetland acidified from ASS (i.e., an affected site) for detailed biogeochemical studies. The results were compared with samples collected from a natural intertidal mangrove forest (i.e., a control site) located within the same wetland. Soil pH (mean: 5.90) indicated acidic conditions in the affected site, whereas pH was near-neutral (mean: 7.17) in the control site. The results did not show statistically significant differences in near-total and bio-available metal concentrations, except for Fe and Mn, between affected and control sites. Iron concentrations were significantly (p values ≤ 0.001) greater in the affected site, whereas Mn concentrations were significantly (p values ≤ 0.001) greater in the control site. However, large proportions of near-total metals were potentially bio-available in control sites. Concentrations of Fe and Ni were significantly (p values ≤ 0.001) greater in leaves and pneumatophores of the affected sites, whereas Mn, Cu, Pb and Zn were greater in control sites. The degree of metal bio-accumulation in leaves and pneumatophores suggest contrasting hydrological behaviors and near-surface geochemical conditions favoring differential metal uptake by mangrove plants in the two sites.

1. Introduction

Mangrove ecosystems are an important feature of coastal estuaries and wetlands, especially in tropical and subtropical regions. These ecosystems serve to protect coastlines from the devastating effects of erosion, storm surges and flooding. Mangrove soils act to sequester metals, which protect coastal marine environments from pollution (Harbison, 1986; Lacerda et al., 1988; Clarke et al., 1998). The ability of mangrove soils to sequester metals is mainly due to the presence of sulfides and organic matter, as well as anoxia, which favor the formation of insoluble metal sulfides and metal-rich organic complexes (Lacerda et al., 1991; Huerta-Diaz and Morse, 1992; Clarke et al., 1998; Zhou et al., 2010). Metal accumulation in intertidal mangrove soils and its partial transference to plant tissues of many mangrove species have been frequently reported (Silva et al., 1990; Lacerda, 1998; Preda and Cox, 2002; Machado et al., 2002; MacFarlane et al., 2003; Lewis et al., 2011; Qiu et al., 2011; Bayen, 2012). Such a role of

* Corresponding author. Tel.: +61 2 9351 6706.
E-mail address: bibhash.nath@sydney.edu.au (B. Nath).

0048-9697/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.scitotenv.2013.06.024

mangrove soils helps to reduce metal transport/exposure to adjacent marine environments.

In estuarine 'mangrove-dominated' environments, trace metal distribution and bio-availability is largely determined by the chemical form of occurrence. Du Laing et al. (2009) have provided a good account of the behavior of different chemical forms of trace metals in estuarine and fluvial systems. The fate of trace metals in estuarine soils is largely controlled by numerous physical, chemical and biogeochemical processes, e. g., land use changes, catchment run-off, tidal behavior and microbial activity (Luoma, 1983; Ferreira et al., 2007a; Du Laing et al., 2009) and these processes vary considerably both spatially and temporally interlinked with coastal hydrological behaviors (Clarke et al., 1997; Bayen, 2012; Nath et al., 2013). Anthropogenic processes, e. g., coastal urbanization, industrial activities, land excavation and agricultural drainage, may trigger Fe- and S-redox transformations by exposing anoxic mangrove soils to atmospheric oxygen (Appleyard et al., 2004; MacDonald et al., 2004; Johnston et al., 2012). Under natural conditions, oxygen may also be introduced into anoxic estuarine mangrove soils through bioturbation or root systems and/or during drying periods and low tide, which may lead to oxidation of sulfides at the soil–water interface (Clarke et al., 1998; Ferreira et al., 2007a; Marchand et al., 2011). Oxidation of sulfidic soils and transformation into sulfuric soils may result in release of acidity and toxic metals or metalloids, such as Al, As and Fe (Dent and Pons, 1995; Clarke et al., 1998; MacDonald et al., 2004).

Mangrove ecosystems are common in coastal flood plains and wetlands of Australia where natural occurrences of acid sulfate soils (ASSs) are commonly reported (Clarke et al., 1998; MacDonald et al., 2004; Keene et al., 2010). These soils are typically formed under reducing conditions beneath the water table, which consists mainly of iron sulfide minerals, such as pyrite (Dent and Pons, 1995; White et al., 1997). These sulfidic soils are normally stable under anoxic conditions and cause no harm to the ecosystem. Generally, production of any acidity within the soil–water interface under estuarine conditions can be quickly neutralized either by the flow of alkaline water or by the buffering capacity of soils (Sammut et al., 1996). However, intense hydrological changes (i.e., alternating inundation–desiccation cycle) associated with natural processes (e. g., oxidation of soils due to bioturbation, drought and low tide) and anthropogenic activities (e. g., land use changes) may induce a large production of acidity and discharge of acidic salts to the estuarine systems (White et al., 1997; Clarke et al., 1998; MacDonald et al., 2004; Johnston et al., 2004; Ferreira et al., 2007a; Amaral et al., 2011a; Nath et al., 2013). The resulting behaviors of estuarine acidification may include fish and oyster kills, fish disease, loss of native vegetation and aquatic biodiversity (Sammut et al., 1996).

There are numerous *Avicennia marina* (Forsk.) Vierh., dominated coastal wetlands in the study area in Lower Hunter Estuary, which have been historically modified by agricultural and industrial activities (Williams et al., 2000). Negative impacts of ASS-induced estuarine acidification on the structure and function of mangrove ecosystems have been previously reported in this area (Amaral et al., 2011a, 2011b). Additionally, mangrove-dominated wetland in Lower Hunter Estuary serves as an important refuge to many endangered and ecologically threatened species and is also a breeding ground for many estuarine animals (NSW DPI, 2008). The wetland also serves as an important habitat for migratory shore birds, green and golden bell frogs (*Litoria aurea*) (KWRP, 2012). However, the impacts of ASS-induced acidification on trace metal distribution, bio-availability and accumulation in mangrove soils and tissues and consequential impacts on the habitats of migratory shore birds, green and golden bell frogs (*L. aurea*) are largely unknown.

Mangrove leaves and pneumatophores were extensively studied to understand metal uptake behaviors and estuarine metal contamination status (e. g., Preda and Cox, 2002; Machado et al., 2002; MacFarlane et al., 2003). The reported metal bio-concentration factor (BCF) was mostly below 1 for leaves when considering total metal concentrations (e. g., Lewis et al., 2011). However, higher BCF values were reported for leaves and other plant organs when considering bio-available and/or weakly-bound metal concentrations (e. g., Machado et al., 2002). Both fine roots and pneumatophores (i.e., aerial roots) have been observed to show greater uptake of metals compared to leaves (Lewis et al., 2011). This is mainly due to physiological differences, variable translocation and excretion mechanisms of different plant organs (MacFarlane et al., 2007; Lewis et al., 2011).

Therefore, the major objective of the present research was to evaluate the behavior of trace metal distribution and bio-availability in mangrove soils. A further objective of the current work was to determine trace metal bio-accumulation and bio-concentration in mangrove *A. marina* (Forsk.) Vierh., leaves and pneumatophores. This study elucidates response to mangrove habitats from changes in environmental conditions due to acidity generation from ASS and to provide knowledge-base recommendations to improve wetland functions and to minimize ecological risks.

2. Materials and methods

2.1. Study site

The study site, Kooragang wetland (Ash Island), is located within the Lower Hunter River Estuary, Newcastle, Australia (Fig. 1). The study site has a legacy of severe human-induced environmental degradation over a period of 200 years due to large scale wetland drainage to sustain agriculture and land clearing for shipping and industrial activities (Williams et al., 2000). The rehabilitation of the wetland has begun in 1993 to restore a natural tidal regime and a habitat for endangered species (KWRP, 2012). The site still has concerns of ASS-induced soil acidification at some locations as a consequence of prior anthropogenic activities. The site has a high ecological value and is listed as a Ramsar category of wetlands (KWRP, 2012). The wetland contains endangered ecological communities and threatened species (NSW DPI, 2008). The wetland also contains mangrove habitats dominated by gray mangrove species — *A. marina* (Forsk.) Vierh., along with salt marsh and freshwater wetlands.

2.2. Sampling — soils, leaves and pneumatophores

Sampling was conducted during September 2012, i.e., at the end of the wet-winter period. Four mangrove plants (i.e., *A. marina*) of similar size and health condition were selected: two plants (plant-1: latitude 32.84632° S and longitude 151.70834° E and plant-2: latitude 32.84602° S and longitude 151.70822° E) were selected at the site which is acidified from ASS (i.e., an affected site), while two plants (plant-3: latitude 32.8473° S and longitude 151.7022° E and plant-4: latitude 32.8472° S and longitude 151.70199° E) were selected in an intertidal natural mangrove forest (i.e., a control site). The affected site was intermittently connected to the estuary through a tidal creek and is affected by alternate wetting and drying cycles depending on the climatic condition. However, the control site was continuously connected to the estuary through a tributary of the same tidal creek.

At the base of each mangrove plant (i.e., plant- 1, 2, 3 and 4) three intact soil cores (~20 cm depth) were retrieved using a push-corer (Birch et al., 2011). The soil cores were taken about 1 m apart at the vertices of a triangular plot with the mangrove plant at the center. Immediately upon collection, the intact soil cores were transferred to an ice box and taken to the laboratory and refrigerated at 4 °C until further processing. Fifteen leaf samples from each plant were collected following the sampling procedure detailed in MacFarlane et al. (2003). Nine pneumatophores of similar size and health condition were also collected from each plant. Samples (leaves and pneumatophores) were stored in a zip-lock plastic bag and transferred to an ice box and taken to the laboratory for preservation at 4 °C until further processing.