Chemosphere 180 (2017) 388–395

Contents lists available at ScienceDirect

Chemosphere

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

Antimony and arsenic exhibit contrasting spatial distributions in the sediment and vegetation of a contaminated wetland

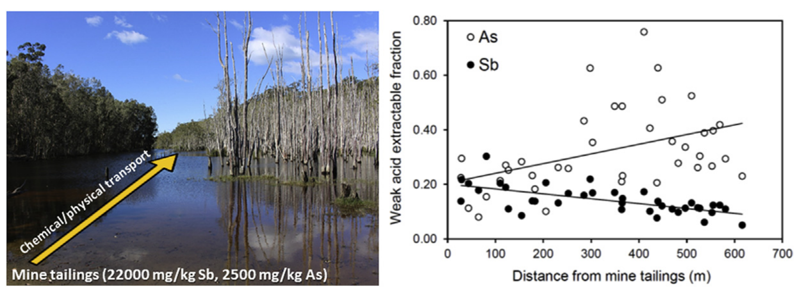
Jan Warnken [a], Rohana Ohlsson [b], David T. Welsh [b], Peter R. Teasdale [c, d], Ariella Chelsky [a], William W. Bennett [b, *]

[a] Australian Rivers Institute, Griffith School of Environment, Griffith University, Gold Coast Campus, QLD 4215, Australia
[b] Environmental Futures Research Institute, Griffith School of Environment, Griffith University, Gold Coast Campus, QLD 4215, Australia
[c] Natural and Built Environments Research Centre, School of Natural and Built Environments, University of South Australia, SA 5095, Australia
[d] Future Industries Institute, University of South Australia, SA 5095, Australia

HIGHLIGHTS

- Spatial dispersion of Sb and As from mine tailings studied in a freshwater wetland.
- Sb was less mobile than As under the prevailing reducing conditions.
- Wetland plants accumulated more As than Sb, despite lower sediment concentrations.
- As presents greater environmental risk due to higher mobility.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 3 January 2017
Received in revised form
17 March 2017
Accepted 26 March 2017
Available online 12 April 2017

Handling Editor: Martine Leermakers

Keywords:
Antimony
Arsenic
Wetland
Sediment
Plants

ABSTRACT

Antimony is a priority environmental contaminant that is relatively poorly studied compared to other trace metal(loid)s. In particular, the behaviour of antimony in wetland sediments, where anaerobic conditions often dominate, has received considerably less attention compared to well-drained terrestrial soil environments. Here we report the results of a spatial assessment of antimony in the sediments and vegetation of a freshwater wetland exposed to stibnite tailings for the past forty years. The concentration of antimony in the sediment decreased rapidly with distance from the tailings deposit, from a maximum of ~22,000 mg kg^{-1} to ~1000 mg kg^{-1} at a distance of ~150 m. In contrast, arsenic was distributed more evenly across the wetland, indicating that it was more mobile under the prevailing hypoxic/anoxic conditions. Less clear trends were observed in the tissues of wetland plants, with the concentrations of antimony in waterlilies (2.5–195 mg kg^{-1}) showing no clear trends with distance from the tailings deposit, and no correlation with sediment concentrations. Sedges and *Melaleuca* sp. trees had lower antimony concentrations (<25 mg kg^{-1} and 5 mg kg^{-1}, respectively) compared to waterlilies, but showed a non-significant trend of higher concentrations closer to the tailings. For all vegetation types sampled, antimony concentrations were consistently lower than arsenic concentrations (Sb:As = 0.27–0.31), despite higher concentrations of antimony in the sediment. Overall, the results of this study highlight clear differences in the behaviour of antimony and arsenic in freshwater wetlands, which should be considered during the management and remediation of such sites.

* Corresponding author.
E-mail address: w.bennett@griffith.edu.au (W.W. Bennett).

http://dx.doi.org/10.1016/j.chemosphere.2017.03.142

1. Introduction

The growing use and demand for antimony (Sb) as flame retardants, lead hardeners and battery or alloy components has pushed annual production to almost 4.2 times the amount of its chemically closest relative, arsenic (As) (U.S. Geological Survey, 2016). The latter has been a priority contaminant for almost a century and its reactions under different environmental conditions are reasonably well understood (Smedley and Kinniburgh, 2002). Knowledge in regard to the reactivity, and therefore mobility and biological uptake, of Sb under different environmental conditions is still developing (e.g. (Tschan et al., 2009; Wilson et al., 2010; Feng et al., 2013; Fu et al., 2016). Existing reviews by Filella et al. (2007), Nakamaru and Altansuvd (2014) and Wilson et al. (2010), and recent work by Fawcett et al. (2015) and Fu et al. (2016) suggest that the mobility of Sb is considerably lower in contaminated soils, even at high concentrations, when compared to As.

Studies investigating Sb dispersion and mobility *in situ* in solid matrices have focused on barren tailing deposits, their surrounding terrestrial soils or stream sediments where samples could be collected using the same methods as for soils (e.g. Okkenhaug et al. (2011); Hiller et al. (2012); Levresse et al. (2012); Fu et al. (2016)). The majority of these matrices were likely to be subject to predominantly oxic conditions and therefore high to moderately high redox potentials.

Sb mobility is known to be influenced by (soil) pore water redox potential (Mitsunobu et al., 2006; Frohne et al., 2011; Hockmann et al., 2014), pH (Leuz et al., 2006b), soil composition and structure (e.g. iron oxides (Leuz et al., 2006a) and Ca (Okkenhaug et al., 2011)), and organic matter content (Steely et al., 2007). Some studies indicate that Sb(III) is less mobile than Sb(V) (Lintschinger et al., 1998; Leuz et al., 2006b). The complexity of the combination and interactions of these factors so far have produced inconclusive results in relation to Sb uptake in higher plants (Feng et al., 2013). In some cases, certain species demonstrated effective exclusion of soil- or pore water Sb, notably in shoots and leaves (e.g. Fu et al. (2016)) while others appear to hyper-accumulate this metalloid in roots and shoots (Feng et al., 2013). A recent investigation of soil contamination with Sb showed a positive, but non-significant trend between soil pH values and Sb bio-accumulation factors (BAFs), indicating low bioavailability under acidic conditions, compared to an inverse trend for As BAFs (and presumably higher bioavailability) in Xikuangshan, China (Fu et al., 2016). These observations, experiments and reviews (Nakamaru and Altansuvd, 2014) suggest that Sb could still be relatively immobile in sediments under anoxic and low pH conditions.

To date, however, few *in situ* investigations have included waterlogged wetland sediments (Nakamaru and Altansuvd, 2014; Fawcett et al., 2015) and to our knowledge no studies have investigated horizontal dispersion in submerged sediments after a major Sb pollution event. In such environments, Sb dispersion will be typically affected by anoxic conditions and low redox potential, as well as high concentrations of humic materials and low pH associated with decomposing plant material. Both, the water column and sediments in such natural wetlands are subject to complex spatio-temporal dynamics (Reddy and DeLaune, 2008) that are difficult to replicate in mesocosm simulations. Oxygen concentrations in these environments, and redox potentials in particular, are affected by diurnal, monthly and seasonal variations in community production and respiration rates, as well as major shifts during heavy rainfalls and floods. Metal(loid) mobility, therefore, is not only the result of a number of physico-chemical and biological processes, but also their time-integrated changes and variations through space. The extent of further impacts of metalloid mobility under such conditions, such as the potential distribution across aquatic and terrestrial food chains, can be initially established from contaminant concentrations in tissues of different types of wetland plants (Cardwell et al., 2002).

This study investigates the two-dimensional spatial distribution of Sb and As in sediments and representative plant species across a semi-enclosed wetland 40 years after a short (4.5 years) but major pollution event associated with the processing of stibnite ore. Tailings were deposited at the inflow section of the wetland, which was located at the end of a small catchment with no other notable sources of Sb. The contaminated site was subsequently closed-off and left undisturbed, without any major rehabilitation works. Under these conditions, the observed Sb and As distributions are considered to be primarily determined by their long-term cumulative biogeochemistry. Detailed examination of these distributions and concentrations of Sb and As in the leaves of waterlilies, sedges and *Melaleuca* sp. trees were used to determine differences in the long-term time-integrated mobility, and risk of persisting contamination, of Sb and As in impacted freshwater wetland sediments under primarily low or stagnant water flow conditions.

2. Materials and methods

2.1. Study site and history

The contamination event that created the conditions investigated in this study occurred in a ~7.5 ha wetland area near the mouth of the Bellinger River in New South Wales, Australia (30°30′20.0″S 153°00′35.9″E). Sb extraction from stibnite ore occurred from 1969 until 1974 on land immediately adjacent to the wetland (Fig. 1). Following separation in a flotation cell, residual tailings were discarded directly onsite without any containment. Aerial photography from 1973 (GHD, 2012) showed tailing deposits occupying an area of ~1 ha, including a section of the main drainage channel. This channel traverses the wetland in a north-east direction and was deepened at some earlier time to establish 'Station Creek', a reserve recorded on the local cadastre. Much of the wetland was cleared for grazing prior to 1969, which showed the creek line on earlier aerial photographs draining eastward across a ledge into a coastal lagoon (Fig. 1). By 1973, the creek line was no longer detectable on black and white aerial photos and much of the site was inundated.

Colour photographs from 1991 showed wetland and vegetation patches very similar to those identifiable on recent high resolution imagery. The wetland is stagnant and depths vary from 0.5 m to 1.0 m in the western (open) section and from 0.5 m to 0 m in the eastern section. The latter was made up of increasingly dense hummocks of sedges and isolated *Melaleuca* sp. trees creating 'islands' and coherent sections above the main water level. A small catchment size (~2.5 km^2), flood lines of a 1:100 flood model and personal observations of water levels after rainfall during field work suggested that water levels and flows were subject to short spikes following local rain events. Mixing with brackish estuarine waters, if any, was restricted to major flood events associated with storm surges and king tides.

The only disturbance of the site occurred in 1980 when a small part of the eastern tailings section and adjoining land were excavated to construct an unfinished L-shaped channel system (Fig. 1). After that event, the site was left fenced off without any notable remediation works.

2.2. Sample collection

This study used a systematic sampling design (SYS, (Wang et al., 2012)). A regular 50 m grid was shifted on top of a rectified aerial photo registered to the local UTM grid (MGA 94 zone 56) using ArcGIS 10.3 to maximise the number of sample sites covering either