Journal of Hazardous Materials xxx (2013) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

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

Effects of nutrient and lime additions in mine site rehabilitation strategies on the accumulation of antimony and arsenic by native Australian plants

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HIGHLIGHTS

- The first investigation of Sb uptake in certain Australian native plants.
- As and Sb transfer from soil to upper plant parts was low (BF ≪ 1).
- Nutrient and nutrient + lime additions increased As and Sb dissolution and plant accumulation.
- Plant species identified for Sb and As contaminated mine soil phytostabilisation.

ARTICLE INFO

Article history:
Received 7 May 2012
Received in revised form 15 October 2012
Accepted 16 January 2013
Available online xxx

Keywords:
Antimony
Arsenic
Plant accumulation
Phytostabilisation
Contaminated soil

ABSTRACT

The effects of nutrient and lime additions on antimony (Sb) and arsenic (As) accumulation by native Australian and naturalised plants growing in two contaminated mine site soils (2735 mg kg^{-1} and 4517 mg kg^{-1} Sb; 826 mg kg^{-1} and 1606 As mg kg^{-1}) was investigated using a glasshouse pot experiment. The results indicated an increase in soil solution concentrations with nutrient addition in both soils and also with nutrient + lime addition for Sb in one soil. Metalloid concentrations in plant roots were significantly greater than concentrations in above ground plant parts. The metalloid transfer to above ground plant parts from the roots and from the soil was, however, low (ratio of leaf concentration/soil concentration ≪ 1) for all species studied. *Eucalyptus michaeliana* was the most successful at colonisation with lowest metalloid transfer to above ground plant parts. Addition of nutrients and nutrients + lime to soils, in general, increased plant metalloid accumulation. Relative As accumulation was greater than that of Sb. All the plant species studied were suitable for consideration in the mine soil phytostabilisation strategies but lime additions should be limited and longer term trials also recommended.

1. Introduction

Hillgrove mineral field in northern New South Wales (NSW) has been a major producer of antimony (Sb) (>60,000 tonnes stibnite concentrates) and gold (Au) sourced from vein and breccia systems containing stibnite and gold associated with arsenopyrite and pyrite. The soils in the mining area are highly contaminated with Sb and also co-occurring arsenic (As) to percent (>1000 mg kg^{-1}) concentrations [1]. Historic mining practices have also resulted in a Sb and As contaminated sediment dispersion plume extending to the coastal floodplain 300 km to the east, where Sb and As concentrations exceed background concentrations over 90% of the floodplain area [2]. This is the largest known anthropogenic dispersion of Sb in Australia.

Current practices for revegetation of disturbed areas at the Hillgrove mine area aim for phytostabilisation, with reduced As and Sb mobility and bioavailability, and reduced erosion and dust generation, rather than phytoextraction of the contaminant metalloids. Native and naturalised plants are used in the rehabilitation strategies with planting directly into soil substrate commonly amended with fertilisers, mulches and lime. In these phytostabilisation strategies, however, uptake and accumulation of the metalloids in plant material presents the risk of active transfer of the contaminants to the wider environment. Using plants that exclude the transfer of the metalloids to above ground plant parts and amendment conditions that reduce plant accumulation offers potential to mitigate this risk [3].

Antimony and arsenic are metalloids that belong to Group 15 of the periodic table. Arsenic has long been recognised as a toxic element [4] but understanding of Sb toxicity and environmental behaviour is more limited [5–7]. Both metalloids commonly occur as oxyanions in environmental systems, either in the +5 oxidation state in relatively oxic environments, or in the +3 state in anoxic environments [6]. The toxicity, behaviour and bioavailability of

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http://dx.doi.org/10.1016/j.jhazmat.2013.01.033

both metalloids in the environment strongly depend on speciation and environmental conditions. Inorganic forms are considered more toxic than organic forms and predominate over organic forms in most environmental systems [8]. Soil pH and redox largely determine metalloid oxidation state. Both metalloids can be strongly retained in soils [9] and the extent of sorption influences the mobile and bioavailable fraction and thence extent of plant accumulation. Many factors influence As and Sb retention in soil but soil pH has an important influence as does the occurrence of co-occurring and competing ions [6]. However, uptake of Sb, but also As, in plants used for revegetation of mine sites in Australia and the effects of soil conditions on the plant accumulation is little studied.

The aims of this work were to understand, using a controlled glasshouse trial, accumulation of Sb and As in plant species successful at colonizing Hillgrove mine site soils and to investigate the impact of different amendment additions used in rehabilitation strategies. The outcomes of the study were intended to target phytostabilisation rehabilitation strategies that enhanced plant colonisation but used plants and amendment mixes that limited metalloid uptake and accumulation.

2. Experimental

2.1. Study soils

Soil was collected from two sites (Site A and Site B) located within the Hillgrove mine area where rehabilitation is currently occurring:

- Site A (30°57′65.70″S, 151°90′14.30″E), created by capping tailings material, has been used for storage and plant equipment prior to rehabilitation works that have been undertaken since 2004. A range of rehabilitation works have been undertaken involving soil ripping and contouring and planting with grass mixtures and native seed with nutrient applications. Natural recolonisation has also occurred on site.
- Site B (30°57′27.90″S, 151°89′95.90″E) is a historic deposition area for inert waste material, which has been capped and covered with soil derived from other areas on site. Site revegetation has used seed bombing with grass species and planting of tube stock seedlings with natural recolonisation also occurring.

2.2. Soil sampling and characterisation

Representative bulk composite soil samples (0–20 cm) were collected from the two sites (Site A and Site B) using a stainless steel spade. The bulked soils sampled were air-dried, thoroughly mixed and sieved to <2.5 mm. Sub-samples were ground to 2 mm and characterised for pH (1:5 soil:water), EC (1:5 soil:water), exchangeable cations, cation exchange capacity, extractable P, total organic C and total Sb and As at a commercial NATA accredited laboratory (Australian Laboratory Services (ALS), Brisbane).

2.3. Glasshouse trial establishment

Plants used in the glasshouse trial included native species that had proved successful for rehabilitation and were already successfully colonizing both sites. These included:

- Couch (*Cynodon dactylon*) that was grown from seed with single tillers planted into the collected soils.
- Tussock Poa (*Poa sieberiana*) that were collected as small tussocks from a background site in the region, trimmed of dead matter, washed with deionised water and single tussocks planted directly into the collected soils.
- *Acacia ingramii* that were purchased as tube stock from a local nursery, washed with deionised water and planted directly into the collected soils.
- *Eucalyptus michaeliana* that were purchased as tube stock from a local nursery, washed with deionised water and planted directly into the collected soils.

Fifteen centimeter diameter pots used for the trial were lined with polyethylene prior to soil and plant addition. The trial was designed as a randomised block design with triplicates of each treatment for each plant in each soil. Treatments included i) no nutrient addition (only for Site A), ii) nutrient addition and iii) nutrient + lime addition. Rates of additions were N (50 kg ha^{-1} at NH_4NO_3), S and K (40 kg ha^{-1} as K_2SO_4), P (10 kg ha^{-1} as $Ca(H_2PO_4)_2$. H_2O which was banded around plant roots) and lime (750 kg ha^{-1} as powdered $CaCO_3$). Supplementary lighting was not used in the glasshouse and the temperature ranged between 15 and 25 °C. The soil was maintained at 80% field capacity with deionised water throughout the 14 weeks of the trial after which the plants were destructively harvested.

Soil solution was sampled in one of the *C. dactylon* replicates for each treatment, only to give a preliminary assessment of As and Sb solution concentrations and to determine whether the sampling method could be used successfully for this purpose. This sampling was carried out at the end of the experiment, prior to plant removal and destruction for analysis, by bringing the soil to field capacity and, after 3 h, drawing the solution into an evacuated tube using a micro-fibre sampler [10].

2.4. Sample analysis

Plant samples were separated into shoots, roots and stems and were washed thoroughly to remove adhering soil with deionised water in an ultrasonic bath, freeze-dried, ground to <1 mm and total As and Sb determined by ALS, using an inductively coupled plasma mass spectrometer (ICP-MS). Soil solution sampled was acidified to pH < 2 and dissolved As and Sb determined by ICP-MS at ALS.

Soil from the rhizosphere was collected, dried at 40 °C, sieved to <2 mm, and total As and Sb determined using a micro-wave aqua-regia extraction procedure with inductively coupled plasma optical emission spectrometer (ICP-OES) detection [11]. The reliability of results was assessed through the analysis of the NIST standard reference material (SRM 2711 Montana Soil). Mean internal standard recoveries for As and Sb were 104% and 93.5%, respectively with a coefficient of variation of <5% for both metalloids.

Statistix 9 and Statistica Version 5 (StatSoft, USA) was used to perform parametric tests. All data was log transformed to provide normality and differences at $p < 0.05$ were considered significant.

3. Results and discussion

3.1. Soil characterisation

Soil characterisation (Table 1) showed that soils were loams at both sites with strong to moderate acidity (pH values of 4.4 and 4.5). Acid mine drainage does not occur at the site due to oxidation of sulfide minerals being buffered by carbonate in the host rock [1]. The organic carbon content of both soils was low (<2%) [12]. Macronutrient and micronutrient availability and CEC was greater on Site B suggesting that soil fertility conditions on this site were more conducive for plant growth. Metalloid soil concentrations at each site were significantly elevated at 2735 mg kg^{-1} Sb and 826 mg kg^{-1} As at Site A and, 4517 mg kg^{-1} Sb and 1606 As mg kg^{-1} at Site B. Background concentrations for the metalloids in the area are typically <7 mg kg^{-1} As and <5 mg kg^{-1} Sb [13].

Please cite this article in press as: S.C. Wilson, et al., Effects of nutrient and lime additions in mine site rehabilitation strategies on the accumulation of antimony and arsenic by native Australian plants, J. Hazard. Mater. (2013), http://dx.doi.org/10.1016/j.jhazmat.2013.01.033