Water Air Soil Pollut (2007) 179:351–364
DOI 10.1007/s11270-006-9238-3

Plant Colonization and Arsenic Uptake on High Arsenic Mine Wastes, New Zealand

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Received: 12 May 2006 / Accepted: 7 July 2006 / Published online: 8 November 2006

Abstract Substrates associated with two historic gold mining sites in north Westland, New Zealand, have locally very high arsenic concentrations (commonly 10–40 wt% As). The substrates consist of iron oxyhydroxide precipitates, and processing mill residues. Waters associated with some of these substrates have high dissolved arsenic (commonly 10–50 mg/L As). Natural revegetation of these very high arsenic sites has occurred over the past 50 years, although some areas of substrate remain bare. Revegetating species include native and adventive shrubs, adventive grasses, rushes, and mosses, and native ferns. Revegetation by higher plants follows initial colonization by mosses, and some shrubs are growing directly in high-arsenic substrate. Shrubs, especially manuka (*Leptospermum scoparium*), gorse (*Ulex europaeus*), tree fuchsia (*Fuchsia excorticata*) and broadleaf (*Griselinia littoralis*) largely exclude arsenic from their shoots (<10 mg/kg dry weight) irrespective of the As content of the substrate. Likewise, most grasses, and reeds (*Juncus* spp.), have only modest As contents (typically <100 mg/kg dry weight). However, mosses growing on high-arsenic substrates have strongly elevated arsenic contents (>0.2% dry weight). In particular, the moss *Pohlia wahlenbergii* acts as a hyperaccumulator, with up to 3% (dry weight) As. Antimony (Sb) contents of all plants are about one thousandth of that of arsenic, reflecting the As/Sb ratio of the substrates. Plant establishment in the high-As substrates may be locally limited by low nutrient status, rather than arsenic toxicity. The shrubs, grasses, and reeds identified in this study are arsenic tolerant and largely exclude arsenic from their shoots so that revegetation with these species, can help to isolate the high-arsenic substrates from the surface environment. These species could be used as phytostabilisation agents on high-arsenic sites that are remote from human habitation. In contrast, the mosses, despite their high arsenic tolerance, are a less desirable component of revegetation of high-arsenic substrates because they actively transfer arsenic from the substrate to the biosphere.

Keywords phytoremediation · phytostabilisation · revegetation · arsenic · antimony · metalloid · hyperaccumulation

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1 Introduction

Mines and mineral processing sites commonly have disturbed land where pre-existing vegetation is cleared and soil is removed or buried (Hutchison & Ellison, 1992; Sengupta, 1993). Commonly, the disturbed land surface becomes enriched in potentially toxic elements, especially metals and/or metalloids, from the ore extraction process (Adriano, 1986; Freitas, Prasad, & Pratas, 2004; Hossner & Hons, 1992; Lottermoser, 2003). These potentially toxic elements can have a negative impact on the immediate environment if they remain exposed for human contact, or physical and chemical erosion of the disturbed land affects nearby streams (Lottermoser, 2003; Sengupta, 1993). Hence, revegetation of mine sites is an important step in site rehabilitation. This revegetation can involve direct planting into the potentially toxic substrate, or addition of capping rock and soil, in which the plants are established (Bruce et al., 2003; Hossner & Hons, 1992; Mains, Craw, Rufaut, & Smith, 2006; Munshower, 1994; Tordoff, Baker, & Willis, 2000).

Revegetation of metalliferous disturbed land at mine sites can have one of two different and mutually exclusive aims: extraction of undesirable levels of elements by plants, or biological stabilization and separation of the high element concentrations from the surface environment (Wong, 2003). The toxic element extraction option, phytoextraction, has had some practical success and considerable potential using hyperaccumulating plants (Brooks, 1983; Ma et al., 2001; Salido, Hasty, Lim, & Butcher, 2003). However, the phytoextraction approach is of limited use when the contaminated substrate is thick (metres to tens of metres). Plants that accumulate environmentally toxic elements, especially hyperaccumulators, are a liability, rather than an asset, for phytostabilisation, as they actively transfer potentially toxic elements from the substrate to the biosphere (Bruce et al., 2003; Freitas et al., 2004; Mains et al., 2006). In these latter situations, provision of a stabilizing plant layer (phytostabilisation) is an alternative and practical approach to site remediation.

This study addresses issues associated with phytostabilisation and specifically avoids phytoextraction as a restoration technique because the amounts and degrees of contamination of affected substrate are large. Identification of plant species suitable for phytostabilisation is best done by observation of plants that naturally colonise the disturbed land of historic mine sites, focusing on species that exclude potentially toxic elements (Baker, 1981; Bradshaw, 1997; Brooks, 1983; Freitas et al., 2004). The present study takes this approach, and examines three different sites at two nearby historic mines: a steep wet forest site, a relatively dry exposed ridgetop, and an associated wetland. All sites have extremely high arsenic concentrations (commonly >10 wt%) in iron oxyhydroxide precipitates, and processing mill residues. The aims of this study were two-fold: (1) to identify plant species capable of naturally colonizing these high-arsenic substrates, and (2) to measure levels of arsenic uptake in different species to identify suitable agents for phytostabilisation of high arsenic sites. Antimony is also locally enriched in our study sites, at much lower levels than arsenic. Antimony behaves chemically in a similar manner to arsenic, so we also report here the antimony contents of plants for comparison to the dominant arsenic.

2 General Setting

The two mines, Globe Hill and Prohibition, that are the focus of this study are on the west coast of the South Island of New Zealand (Figure 1). Both mining areas receive c. 2,300 mm mean annual precipitation, and rainfall can occur all year round. Mean annual temperature is 12 °C. Dense rainforest originally clothed the steep terrain, and forest has regenerated over much of the mined areas since mining ceased more than 50 years ago. The two mining areas are now

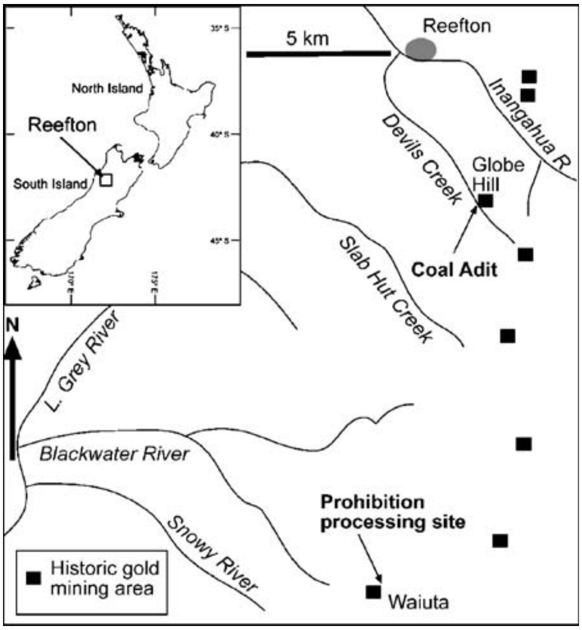

Figure 1 Location map showing the two studied mine sites, and other historic gold mining areas, in the Reefton area, north Westland. *Inset* shows the north Westland area in the South Island of New Zealand.

unpopulated, but intensive agriculture occurs downstream of the mine sites. Most regenerated forest is dominated by southern beech (*Nothofagus* spp.), but early stages of forest regeneration have abundant shrubs, particularly manuka (*Leptospermum scoparium*) and kanuka (*Kunzea ericoides*). Soils in regenerated forest areas typically have pH between 5 and 6, and many surface waters have similar pH. However, groundwater in the underlying basement typically has pH near 7 (Hewlett, Craw, & Black, 2005).

Both mines extracted gold from mineralised structures in the Ordovician metasedimentary rocks (Christie & Brathwaite, 2003). The mineralised structures have abundant (up to 1 wt%) arsenopyrite (FeAsS) associated with the gold, and that arsenopyrite was extracted with the gold, or was exposed by mining operations. Likewise, stibnite (Sb_2S_3) occurs locally in the ore. Hence, the disturbed land in the vicinity of the mines is enriched in arsenic (As) and antimony (Sb), and waters draining from the mined areas have elevated As and, to a much lesser extent, Sb (Hewlett et al., 2005).

The high-arsenic substrates examined in this study arose from different mine-related processes. Iron-rich precipitates with elevated As and Sb levels are common where mine waters emerge from underground tunnels, and one such deposit at Globe Hill (Figures 1 and 2) is a site considered in this study. The second site was a

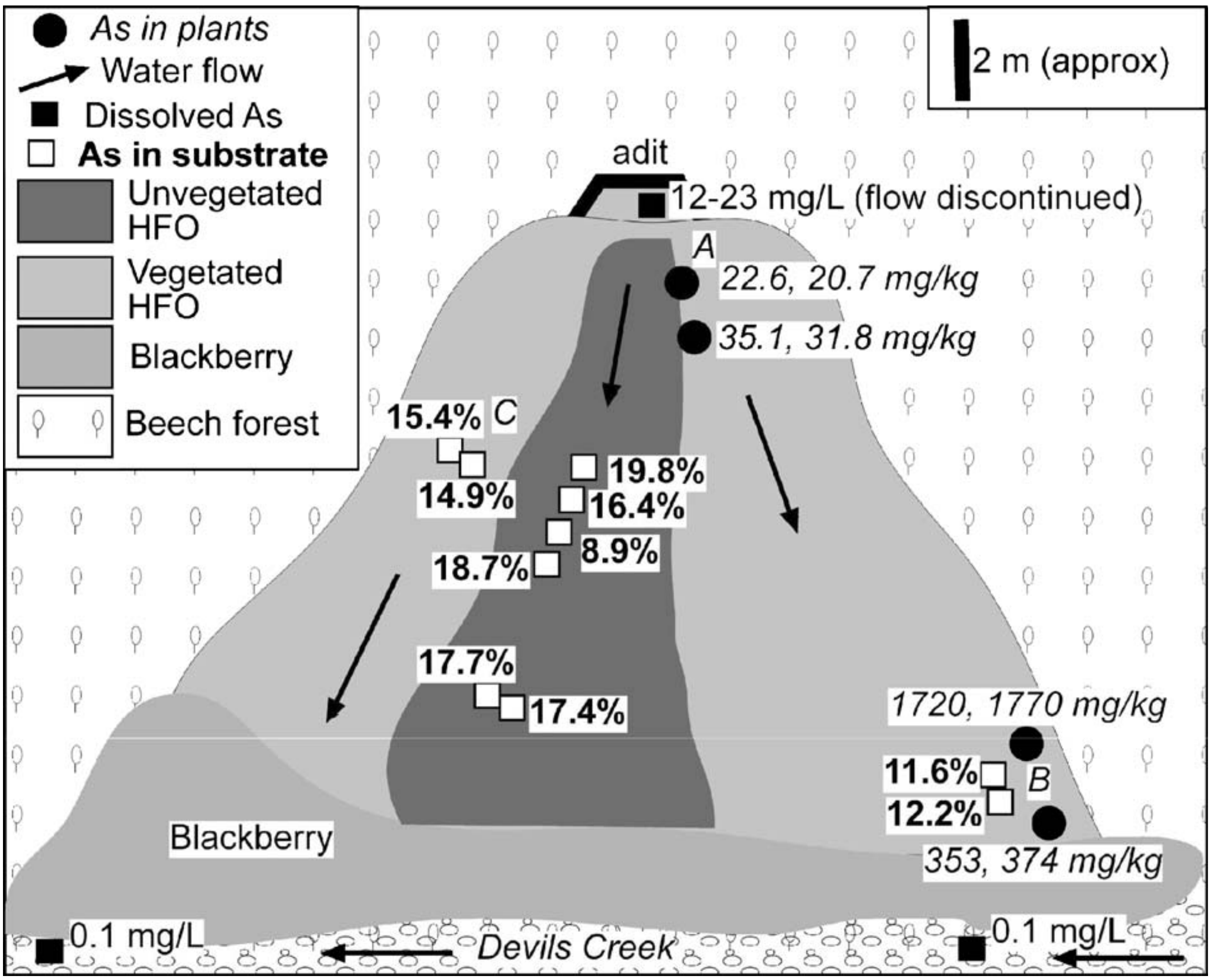

Figure 2 Sketch map, based on a photograph and field sketches, of the HFO fan emanating from an adit (*top*) associated with the Globe Hill gold mines, and extending down to Devils Creek (*bottom*). Different shading represents different degrees of revegetation, as indicated. Plant identification and sample areas are indicated with *letters* (see Table I). Arsenic contents of plants (*filled circles*; species in Table I), water (*filled squares*), and HFO substrate (*open squares*) are annotated on the sketch. Water drainage directions are indicated with *arrows*.

processing mill near Waiuta (Figure 1), where ore concentrates rich in arsenopyrite were roasted to liberate the fine grained gold. Arsenic-rich residues, with minor Sb, were discarded nearby, and it is these residues that are investigated at the Prohibition mine processing site and adjacent wetland (Figures 1 and 3). Post-mining rehabilitation was not undertaken on disturbed land at either site, but natural colonization has occurred from surrounding seed sources.

3 Study Areas

Mining of gold at Globe Hill (Figure 1; lat 42°10.12′S, long 171°53.18′E) began in 1870 and ceased in 1920 (Christie & Brathwaite, 2003; Latham, 1992). The mine complex consisted of two shafts and a network of tunnels on 11 levels (Henderson, 1917) inside a hill with 150 m of steep relief above a deep gorge of Devils Creek (Figures 1 and 2). Coal to drive the equipment was brought in to the base of the mine, from a nearby coalfield, through a tunnel (Coal Adit) near to Devils Creek. When the mine was closed, ground water in the mine tunnels discharged through the Coal Adit to Devils Creek (Figure 2). The discharging water had a high content of dissolved iron and arsenic, and some of this precipitated on oxidation at the entrance to the Coal Adit. The precipitates are dominated by iron oxyhydroxide (HFO) that have built up a half-cone shaped fan between the adit entrance and the river (Figure 2). The regenerated forest surrounding the HFO fan is dominated by *Nothofagus menziesii* and *N. fusca* trees up to 10 m tall, with an understorey of shrubs, mainly *Griselinia littoralis* (Table I). The forest floor has scattered moss and fern species.

The water discharge down the HFO fan ceased in the late 1990s when a new exploration drilling programme diverted this water out some drill holes. The drillhole water has up to 23 mg/L As and 0.07 mg/L Sb (Figure 2; Craw, Wilson, & Ashley, 2004; Hewlett et al., 2005). Groundwaters that originally contributed to the formation of the HFO define HFO fan, and the water in Devils Creek, have pH near to 7 (Hewlett et al., 2005). The fan of precipitated material at the Coal Adit entrance at Globe Hill (Figure 2) is orange-brown in colour, and is dominated by iron oxyhydroxide (HFO). Secondary seams and patches (mm scale) of pharmacosiderite ($K_2Fe_4[AsO_4]_3[OH]_5.6.3H_2O$) occur in places through the HFO (Hewlett et al., 2005). The HFO is finely laminated (mm scale) parallel to depositional slopes, and it incorporates abundant plant leaves (ca 5% by volume) from trees in surrounding regenerating forest. Paste pH measurements of the HFO fan material range from 7 to 7.5. Water and substrate composition data from Craw et al. (2004) and Hewlett et al. (2005) for the Globe Hill mining area are included in this study where appropriate.

The Prohibition mine and processing mill (Figures 1 and 3; lat 42°17.49′S, long 171°49.64′E) is on the crest of a ridge, 120 m above the surrounding valley. The processing mill treated ore from the nearby underground mine from 1938 to 1951 (Latham, 1992). A heavy mineral concentrate rich in arsenopyrite was made in the mill, and heated in an Edwards roaster. Exhaust gases from the roaster precipitated arsenic-bearing oxides, mainly arsenolite (As_2O_3), in several condenser chambers, of which the condenser tower is still standing. Some of this condensate was discarded outside the processing plant. Remnants of this condensate, and other processing plant residues, now coat the ground surface in the immediate vicinity of the processing plant ruins (Figure 3). Some of the arsenolite has transformed to scorodite in the substrate, although crystals of arsenolite still persist near the condenser. Paste pH of the As-rich substrates around the processing site range from 3 to 5.

The wetland immediately below the processing plant site was originally a tailings impoundment behind a dam at the northern end (Figure 3). This impoundment has developed into a vegetated wetland since the site was abandoned. Almost no open water remains except irregular patches (30 cm scale) near the centre of the wetland (site D, Figure 3). Larger areas of open water occur temporarily during major rain events, but these drain away within hours. Elsewhere, the wetland surface consists of variably saturated vegetation mats overlying a substrate of processing plant residue and sediment washed off the surrounding slopes. Water pH in the upper 10 cm of the wetland varies on the metre scale between 4.0 and 5.2.

4 Methods

4.1 Units

The arsenic analytical data obtained in this study span an extremely wide range (8 orders of magnitude) from

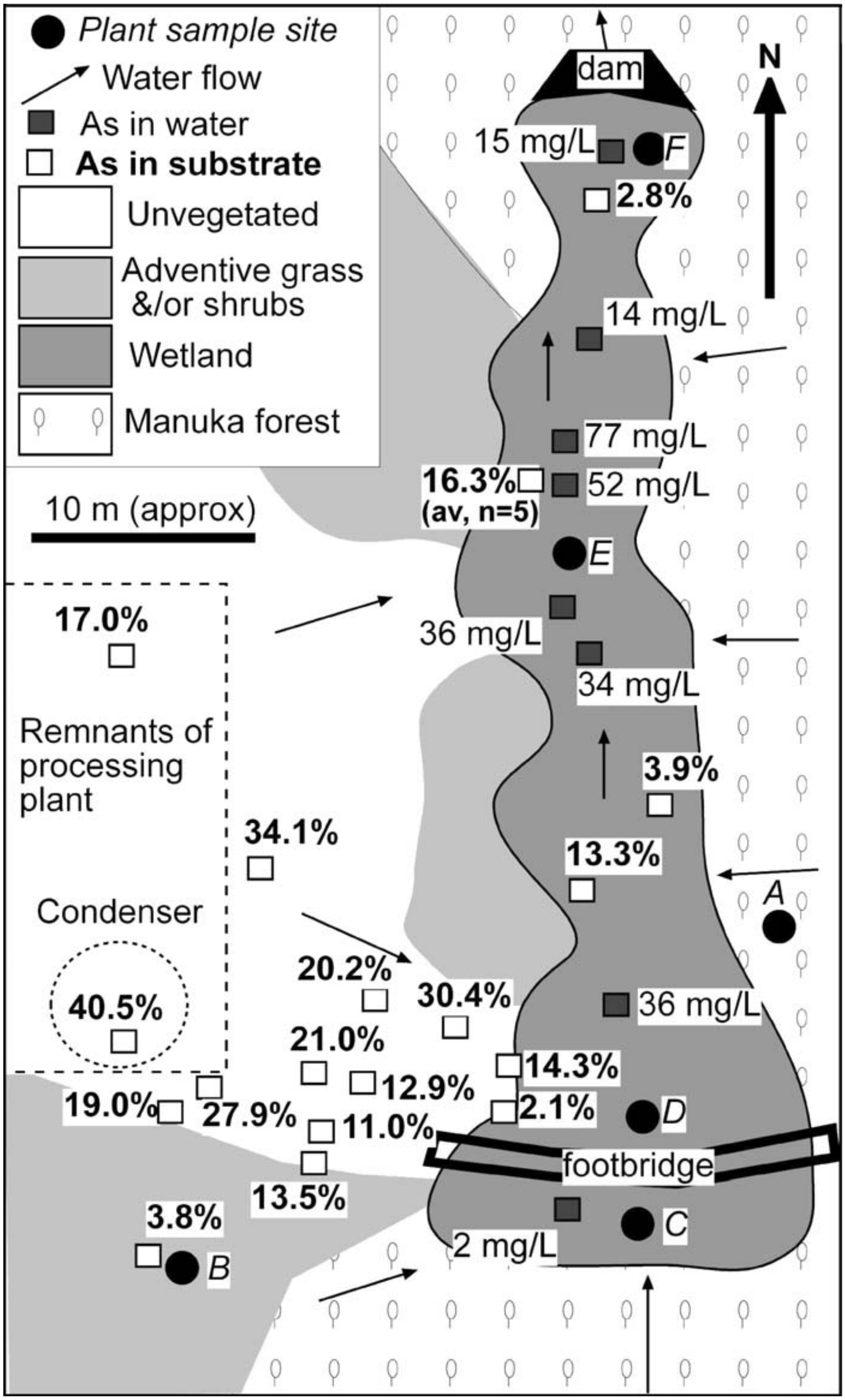

Figure 3 Sketch map, based on field sketches and oblique photographs, of the Prohibition processing mill site (*left*) and adjacent wetland (*right*). Different *shading* denotes different degrees and types of revegetation. Plant sample sites are indicated with *filled circles* (species and analyses in Table II). Arsenic contents of waters (*filled squares*) and substrates (*open squares*) are annotated on the sketch. Water drainage directions are indicated with *arrows*.

near instrumental detection limits to major-element levels. No one unit is ideal for this very wide range of analytical data. Hence, we use mg/kg (= parts per million) for relatively low concentrations, and weight % for relatively high concentrations. We allow some overlap of the ranges of use of these units, depending on the context, particularly in the range 0.1 to 1 wt% (1,000 to 10,000 mg/kg). We have used mg/kg throughout Tables I and II, and in Figure 4 for internal consistency and ease of comparison.

4.2 Plants

Common plant species growing on the substrates under investigation were identified in the field. Species of less certain identity, including all mosses, were sent to Manaaki Whenua Landcare Research N. Z. for formal identification. Samples of individual species taken for chemical analysis were collected from representative portions of above ground foliage (leaves and attached soft stems). When possible, two field samples per species were collected. At the Prohibition site, naturalised grasses of several species were intergrown with minor small forb species, so these were collected as composite samples. Plant species with low field biomass were not sampled. The majority of foliage samples were collected in the austral autumn 2005 but repeat collections of some species were also carried out in winter 2005 at the Prohibition site.

Sampling of plant shoots for chemical analysis was restricted to large specimens because of the difficulty in cleaning the fine grained HFO off material from small specimens. All plant material was washed thoroughly several times with tap water to ensure that contaminant inorganic material was not attached. Particular care was taken in the washing stage with the moss samples because of their close proximity to the substrate. The plant material was then rinsed finally with distilled water, before being dried in an oven at 50°C. Two separate sub-samples from the material of each species, or species mix, were prepared for analysis. The dried plant material was further dried before grinding in a steel grinder at Hill Laboratories, Hamilton, New Zealand, an internationally accredited laboratory. The ground plants were digested in nitric and hydrochloric acid and the digest solution was analysed for As and Sb by ICP-MS. Detection limits for these analyses are 0.1 mg/kg for As and 0.02 mg/kg for Sb.

A moss sample was prepared for examination by electron microprobe (JEOL JXA-8600) by directly

Table I Plant species naturally established on a HFO fan at Globe Hill, Reefton, with associated levels of arsenic (As) and (Sb) in foliage (values represent range of two samples per species) collected in May 2005

Species Name	Common Name	Element	Sampling Sites		
		mg kg^{-1}	Flat top A	Upstream Slopes B	Downstream Slopes C
Fuchsia excorticata	Tree fuchsia	As Sb	31.8–35.1<0.02	•	•
Nothofagus fusca	Red Beech		•	•	
Nothofagus menziesii	Silver Beech		•	•	
Griselinia littoralis	Broadleaf	As Sb	20.7–22.6<0.02		
Coprosma foetidissima	Stinkwood		•		
Astelia fragans	Bush flax		•		
*Rubus fruticosus**	Blackberry				•
Blechnum discolor	Crown fern	As		353–374	
		Sb		0.04–0.08	
Polystichum vestitum	Prickly shield fern				•
Hypolepis rufobarbata	Filmy fern				•
Blechnum sp.	Palm-leaf Fern			•	
Blechnum sp.	Common Hard Fern			•	
*Heteroscyphus coalitis**	Moss	As		1,720–1,770	
		Sb		0.2	
*Marchantia foliacea**	Liverwort				•

N.B. •=species present but not collected for analysis; *=adventive species. Refer to Figure 2 for location of sampling sites.

Table II Plant species naturally established at Prohibition Mine, Waiuta, and associated levels of arsenic (As) and (Sb) in foliage (values represent range from two samples) collected in May 2005

Species	Common Name	Element	Sampling Sites						
			Background Soil	Processing Mill	Wetland				
		mg kg^{-1}	A	B	C	D	E		F
Leptospermum scoparium	Manuka	As	1		2.7–3.1		autumn	winter	3.5–3.6
		Sb	0.03		<0.02				<0.02
*Ulex europaeus**	Gorse	As			2.0–2.2	4.2–4.6			
		Sb			0.03	0.02			
See below*[a]	Wild grass mix	As		10.3–11.1	7.6–8.3	27.2–38.8	69.6–83.3	289–801	
		Sb		0.03–0.05	0.03	0.08–0.11	0.14–0.15	0.32–1.04	
*Juncus articulatus**	Jointed Rush	As					69.8–74.6	108–111	
		Sb					0.05–0.09	0.11–0.17	
*Juncus effuses**	Soft Rush	As			3.0–3.2	6.4			
		Sb			0.02–0.05	0.06–0.07			
Juncus prismatocarpus					•				
*Pohlia wahlenbergii**		As					29,000–30,800	2,170–28,800	
		Sb					126–128	62–145	
*Campylopus pyriformis**				•		•			

[a] *Agrostis capillaries** (Browntop), *Holcus lanatus** (Yorkshire fog), *Anthoxanthum odoratum** (Sweet vernal), *Hypochoeris radicata** (Catsear), *Plantago lanceolata** (Plantain), *Trifolium subterraneum** (Subclover), *Ranunculus repens** (Buttercup), *Lotus pedunculatus** (Trefoil).

N.B. •=species present but not collected for analysis; * = adventive species; repeat collections for wild grass mix (n = 4), *J. articulatus* (n = 3) and *P. wahlenbergii* (n = 6) taken in winter 2005. Refer to Figure 3 for location of sampling sites.

gluing stems on to a sample holder, and by embedding stems in resin and polishing the top surface to reveal oblique sections through the stems. Both mounts were carbon-coated to ensure conduction of electrons. The mounts were examined with a defocused beam at 15 kV, and secondary electron images were obtained, which show variations in surface topography of the samples. Arsenic X-ray responses to electron irradiation appear as white dots on images, detected by wavelength dispersion spectrometry over 20 min. Background effects were shown to be negligible by analyzing for Sb (known to be at low levels), and Cu (not enriched in these substrates). The detection limit for As in rock material via wavelength dispersion on the microprobe is ca 0.1 wt%, and the detection limit is lower (but unknown) on plant material. This microprobe technique is less sensitive than micro-PIXE (Ohnuki et al., 2002), but adequate for the high concentrations observed in this study.

4.3 Substrate and water

Substrate samples were collected from the upper 10 cm using a spade and placed in clean plastic bags. At each site, samples were collected from both vegetated and unvegetated substrate around the point source of contamination (Figures 2 and 3). At the Prohibition site, substrate samples were also collected along a transect through the wetland (Figure 3). After drying at 50 °C, the samples were ground to fine powder with an agate mortar and pestle. Two separate sub-samples from each individual collection were prepared for analysis. All samples were sent to Hill Laboratories, where they were digested with nitric and hydrochloric acid before analysis by ICP-MS (US EPA method 200.2). Detection limits are 2 mg/kg dry wt for As and 0.4 mg/kg dry wt for Sb.

Samples of water were collected from pools in hollows between vegetational mounds in the Prohibi-

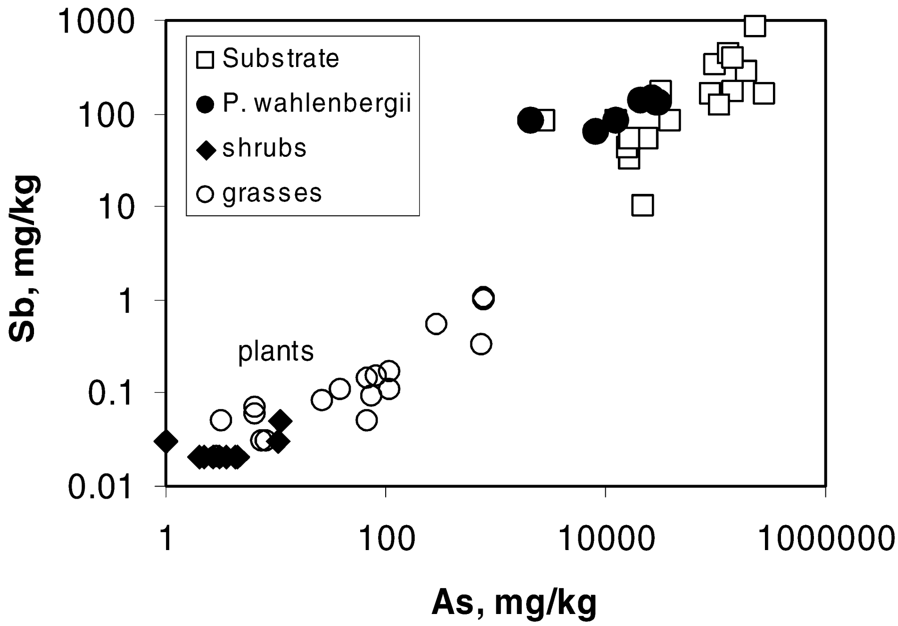

Figure 4 Comparison of arsenic and antimony contents of substrates (*open squares*) and plants (*other symbols* as in legend) at the Prohibition processing plant and wetland.

tion wetland. These water samples were collected in acid-washed plastic bottles along a transect down the wetland, at sites close to the plant and substrate samples (Figure 3). One initial sample was collected without filtration, and later samples were filtered (0.45 μm). The waters were analysed by ICP-MS at Hill Laboratories. Detection limits are 0.001 mg/L for As and Sb.

5 Results

5.1 Globe Hill, Reefton

The HFO fan at Globe Hill contains variable proportions of As. Arsenic levels in unvegetated substrate were typically 9–20 wt%, and in vegetated substrate were 12–15 wt% (Figure 2). The unvegetated strip down the centre of the fan is where the discharging water flowed immediately before flow ceased in the 1990s. Up to 8 mg/kg Sb is dispersed through the HFO and occurs as discrete amorphous zones (Hewlett et al., 2005).

The flat top of the HFO fan adjacent to the adit has been colonized by forest species, with abundant individual trees up to 5 m tall (Table I). Moss and ferns are scarce. The vegetated slopes of the HFO fan have abundant moss, ferns and liverworts, with scattered shrubs and trees (Table I). A small patch (2 m^2) of *N. menziesii* and *N. fusca* (silver and red beech) saplings has developed on the upstream slopes. The vegetation cover is denser on the upstream slopes than the downstream slopes. Most of the colonizing plants are locally occurring native species, but minor adventive liverwort, moss, and blackberry are present locally (Figure 2, Table I).

Moss was the most abundant plant life form on the HFO fan. Where it grew alone, moss caused little disruption of the underlying substrate, essentially coating the depositional surface. In some places, ferns have colonized the mossy surfaces, with roots of larger ferns extended down into the HFO for up to 30 cm. Fern root establishment has disrupted the upper 5–10 cm of HFO substrate, but below this, the original depositional layering is preserved. Shrubs also appear to have colonized mossy surfaces. Their roots extend laterally for at least 1 m in the upper 20 cm of the HFO, and one *Fuchsia excorticata* (tree fuchsia) individual with a 20 cm diameter trunk was deeply rooted within the HFO.

Samples of small branches and attached leaves from *F. excorticata* and *G. littoralis* (broadleaf) shrubs growing in HFO had <36 mg/kg As (Table I). Leaves from large *Blechnum discolor* (crown fern) had up to 374 mg/kg As, and leaves from the moss species *Heteroscyphus coalitis* up to 1,800 mg/kg As (Table I). Antimony levels of all plant species tested were low (≤0.2 mg/kg; Table I).

5.2 Prohibition mine, Waiuta

5.2.1 Processing Mill Site

The substrate around the old mill site typically contains ca 20 wt% As, although concentrations as high as 40 wt% were recorded (Figure 3). The amount of As in the substrate decreases over 10–30 m away from the condenser (Figure 3). The Sb content of this substrate varied from 10 to 1,000 mg/kg (Figure 4).

Post-mining revegetation of the site was less developed than at Globe Hill (above), and dominated by herbaceous, adventive species (Table II). The area immediately around the mill (ca 500 m^2) is largely bare of vegetation, although some isolated clumps of *Agrostis capillaris* (browntop) and *Hypochoeris radicata* (catsear) have established. Small patches (<1 m^2) of moss (*Campylopus pyroformis*), locally in combination with *A. capillaris*, *Holcus lanatus* (Yorkshire fog) and *H. radicata*, have developed on small, brown silicate-rich deposits embedded within the predominantly bare grey arsenolite/scorodite-rich substrate. The silicate-rich substrate had relatively low As content (<5 wt%). Beyond the immediate area around the mill to the south, a narrow (10–20 cm) zone of moss (*C. pyroformis*) further defined the boundary between more extensive silicate-rich deposits and adjacent arsenic-rich substrate. Strips of the moss boundary have died in places, leaving a brown organic layer ca 2 cm thick. A dense cover of intergrown grass and forb species has developed on the silicate-rich substrate (Figure 3). Foliage samples from this wild grass mix (site B) contained up to 11 mg/kg As (Table II; Figure 3). Foliage samples from a dense native stand of *L. scoparium* (manuka) growing in soil (site A) on slopes 30 m away contained 1 mg/kg As (Figure 3; Table II).

5.2.2 Wetland

The substrate in the Prohibition mine wetland had variable but locally strongly elevated As contents (Figure 3), which were generally lower than those of the dry substrate surround the processing plant (above). The highest As contents were beneath the wettest part of the wetland, near plant sampling site E (Figure 3). Seven substrate samples taken in this area had average As content near 16% (Figure 3), but ranged between 2.4% and 23%. The Sb concentration of substrates was low (80–800 mg/kg), but elevated above background rock contents because of the presence of stibnite in some ore (Christie & Brathwaite, 2003).

Arsenic concentrations of waters in the wetland also ranged widely, from 14 to 77 mg/L, with the highest values obtained in waters in the wettest part of the wetland (near plant sample site E; Figure 3). The 77 mg/L As concentration was recorded from an unfiltered sample, and a repeat (filtered) sample from nearby 3 months later yielded 52 mg/L As. Since the second sample was taken after rain, it is not clear whether or not the difference between these samples was a result of dilution of the later sample, or particulate As material in the first sample.

Vegetation in the driest parts of the wetland (north and south ends; plant sampling sites F and C; Figure 3) was dominated by adventive grasses and scattered native *L. scoparium* shrubs. Minor adventive *Ulex europaeus* (gorse) shrubs occurred as well. Progressively wetter portions of the wetland showed increasing abundance of *Juncus* spp. (rushes). Fully saturated patches, including those with open water pools, contained the adventive *Juncus articulatus* in combination with moss. Large, dense mats of the adventive moss *Pohlia wahlenbergii* formed in and around ponds of open water, particularly near plant sample site E (Figure 3).

The *L. scoparium* shrubs growing in the wetland had slightly higher As levels (ca 3 mg/kg) than those growing on adjacent soil (Table II). Arsenic contents in *U. europaeus* shrubs and *Juncus effusus* were also relatively low (<7 mg/kg), but levels in plants growing downslope from the mill (site D) were twice that of those growing upslope respectively (site C Figure 3; Table II). Arsenic amounts in the wild grass mix also increased downstream through the wetland from ca 8 mg/kg to up to 803 mg/kg (Table II). Grass samples collected in winter 2005 contained much higher As and Sb contents than samples collected in autumn 2005 (Table II). *J. articulatus* samples also contained elevated As contents in winter compared to autumn, up to 111 mg/kg. Antimony concentrations of the wetland plants were generally low (<1 mg/kg) apart from *P. wahlenbergii* moss (see next section). There was a generally consistent ratio between As and Sb concentrations which was similar to that of the substrates, although plants generally had lower levels of both metalloids (Figure 4).

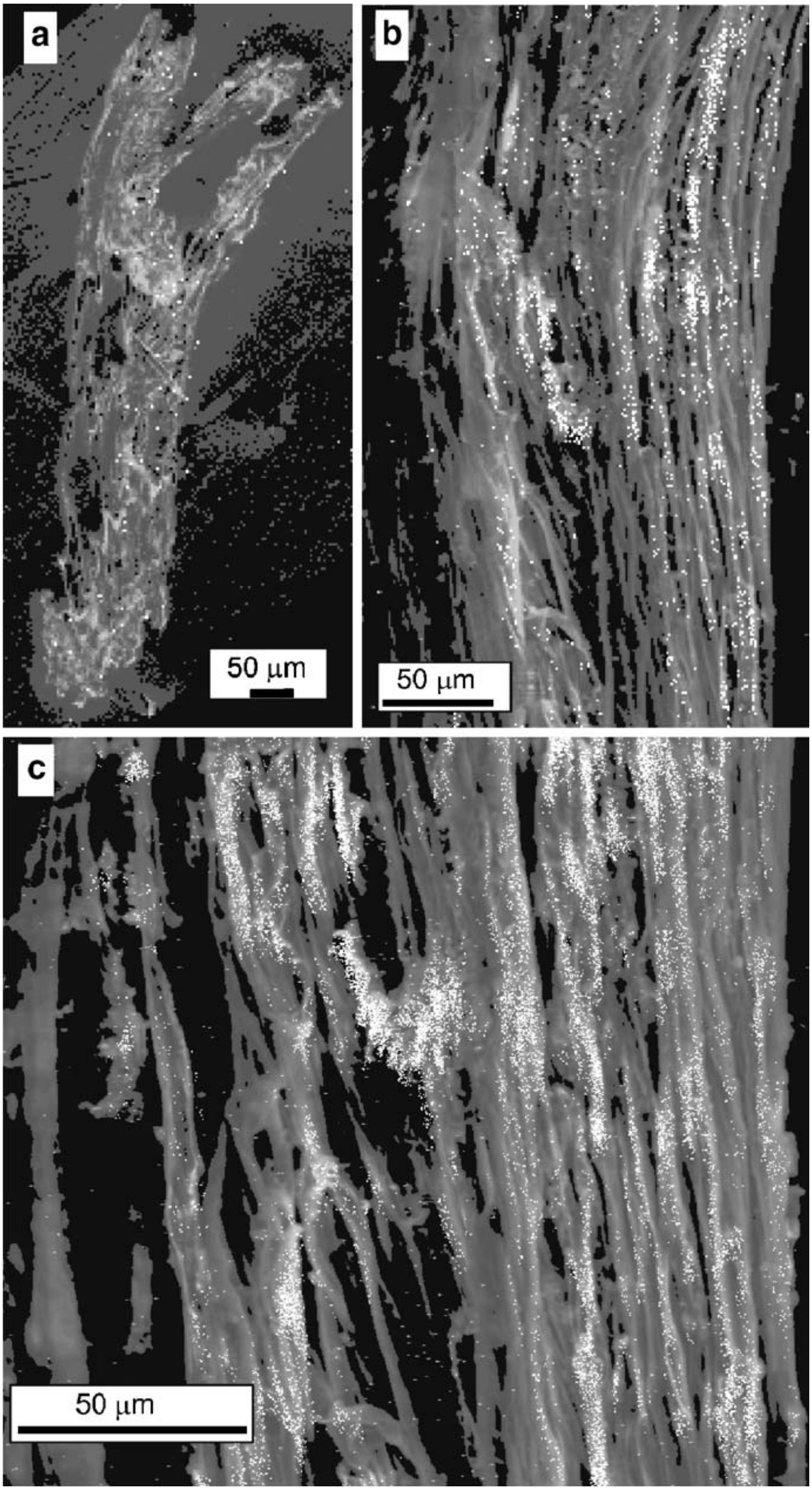

Figure 5 Secondary electron images of stems of moss (*Pohlia wahlenbergii*) from the Prohibition wetland (see text for preparation and operating conditions). *Small white dots* over the moss are As X-rays detected by wavelength dispersion. (a) Oblique section through a stem embedded in resin. X-ray dots are only just visible at this scale. (b) and (c) Moss stem glued to a sample mount, with accumulations of As X-rays in patches over the topographically higher zones.

Analyses of the moss *P. wahlenbergii* from the wettest part of the wetland (site E) were consistently high in As, up to 3 wt% (Table II). The Sb content was also relatively high (up to 145 mg/kg) compared to other plants analysed in this study (Table II). These high As and Sb values were similar to some of the inorganic substrates, and the As/Sb ratio is similar to the substrates as well (Figure 4). To ensure that these high metalloid contents were not a result of contamination by inorganic substrate material, fragments of one sample were examined in detail with an electron microprobe. Contaminant material, if present, would be readily visible adhering to the outside of moss stems. No such contaminant material was observed. Instead, the As occurred distributed throughout internal moss structures (Figure 5a–c). The distribution of As-induced dots is variable because the electron microprobe detects X-rays emitted from the topographic high portions of the sample (light-coloured, Figure 5a–c). X-rays emitted from other parts of the sample are absorbed by the sample material, or are emitted at an angle that is not received by the detector. We conclude that the internal structure of the moss is As-rich, similar to observations made by Ohnuki et al. (2002).

6 Discussion

6.1 Site revegetation

Natural revegetation of disturbed land at historic mine sites is an effective and relatively low-cost management strategy (Bradshaw, 1997), and the present study shows that revegetation has been occurring naturally at all the studied sites. Most of the surface of the HFO fan at Globe Hill has been colonized by plants and this colonization has occurred progressively throughout the >80 year development of the fan. Early stages of colonization were buried by subsequent precipitation, and remnants of these plants are preserved, with fallen leaves, as localized organic layers (cm scale). The plants on the current surface therefore represent the most recent stages of colonization, although the exact timing of this colonization is not known. This natural revegetation can occur on material that has up to 15 wt% arsenic and possibly higher (Figure 2). Some of the revegetation at this site probably occurs initially by colonization of mosses that in turn provide a suitable growing medium for ferns and, ultimately, forest trees. However, substantial and healthy native trees (*F. excorticata*, *G. littoralis*) were also growing directly in the arsenic-rich substrate near the top of the HFO fan (Figure 2). Clearly, these trees derive sufficient nutrients from the substrate and are apparently not affected by the high arsenic concentrations.

Although amounts of As were generally higher in unvegetated than vegetated parts of the Globe Hill HFO fan, the unvegetated substrate also corresponded with the course of most recent water discharge from the Coal Adit. Therefore, it is likely that disturbance, and physical parameters, of the substrate could explain the absence of plants, rather than arsenic phytotoxicity. Nutrients for plant growth may be supplied by decomposition of leaf litter that became incorporated into the HFO fan during its build-up. No attempt was made to determine the nutrient status of the HFO because, with up to 20% arsenic, this material is potentially toxic to laboratory workers.

Like the Globe Hill HFO fan, the high As of the Prohibition wetland is apparently not a hindrance to natural revegetation as plants cover nearly all the surface. Substrate As contents in the Prohibition wetland were typically <16%, but some waters in the wetland had very high As contents, up to 77 mg/L (Figure 3). Here, the moss *P. wahlenbergii* formed dense and expansive mats (around plant sampling site E; Figure 3). Growth of a similar species, *Pohlia nutans*, has been shown to be little affected, or possibly even enhanced, by strong metal pollution (Gilbert, 1971; Huttunen, 2003). In addition, given that the growth of *P. wahlenbergii* is also strongly nutrient limited (Sandvik & Heegaard, 2003), it appears that adequate nutrients are available in the wetland to facilitate plant establishment.

In contrast to the Globe Hill and Prohibition wetland sites, observations at the Prohibition processing mill site showed that natural revegetation has not occurred on the most arsenic-rich substrate (typically 20–30 wt% As; Figure 3). The sharp boundary between arsenic-rich unvegetated substrate and lower-arsenic (<5%), silicate-rich vegetated substrate at this site indicates that substrate chemistry is a likely controlling factor of revegetation. The lack of plant colonisation on high-arsenic substrate may be a result of arsenic toxicity, or because the low pH (as low as 3) inhibits plant uptake of the limited nutrients that are available, or some combination of these (Bradshaw, 1997). The other two sites examined in this study show no signs of arsenic toxicity at substrate concentrations approaching and/or overlapping with those of the processing plant site. Hence, we suggest that arsenic toxicity is not limiting the establishment of plants on the Prohibition processing plant site. Other possible factors such as substrate texture, water holding capacity, or nutrient status in general may be hindering plant colonization. No nutrient status data were obtained from this site because of the high toxicity of the substrate in the laboratory, so it is not possible to further resolve this issue.

6.2 Site remediation

The natural revegetation summarised in the previous section is progressively providing a natural cover to some extremely arsenic-rich material that is of high toxicity to humans. Plants are progressively isolating this toxic material from the surface environment. However, the degree to which the arsenic-rich substrate is separated from the surface biosphere is governed by the amount of arsenic that the various plants incorporate into their structure (Meharg & Hartley-Whitaker, 2002). All the observed species in this study are clearly arsenic-tolerant, but some species take up more arsenic than others.

The analyses of plants listed in Tables I and II provide some indications of the relative usefulness of the various species for site remediation. For example, the native shrub manuka (*L. scoparium*) apparently excludes arsenic very effectively, despite growing on substrate with nearly 3 wt% As, and dissolved As of 15 mg/L in wetland water (Figure 3; Table II). Adventive gorse shrubs (*U. europaeus*) are similarly effective at excluding arsenic (Figure 3; Table II). Native fuchsia and broadleaf shrubs (*F. excorticata*, *G. littoralis*) absorb only minor amounts of arsenic (up to 35 mg/kg) while growing on substrate with more than 10% arsenic (Figure 2; Table I), so these species are also remarkably effective at excluding arsenic. Similarly, the adventive *Juncus* rush species in the wetland can exclude arsenic effectively (Figure 3; Table II). Even in the most arsenic-rich part of the wetland, with substrate As of ca 16% and dissolved As >50 mg/L in waters, *J. articulatus* absorbed only modest amounts of arsenic (up to 111 mg/kg; Table II). Crown ferns (*B. discolor*) take up intermediate levels of As (300–400 mg/kg; Table I).

The adventive grass mix that was common at both the studied Prohibition sites appeared to exclude arsenic with varying degrees of effectiveness. In the extremely arsenic-rich environment of the wetland mentioned above, As levels in the grass species mix sampled in autumn were less than 90 mg/kg As, yet were up to 800 mg/kg when sampled in winter. Further work is required to determine reasons for such a discrepancy in the data. Arsenic concentrations have been shown to vary in leaves versus stems (Robinson, Duwig, Bolan, Kannathasan, & Saravanan, 2003; Smith, Naidu, & Alston, 1998), as well as in live versus dead leaves (Porter & Peterson, 1975). Consequently, if samples from different collection periods contained variable proportions of different structures, this could affect the As content outcomes. Similarly, if different proportions of species were contained in the composite samples, this could also vary the data given that As uptake can vary among different grass species (Mains et al., 2006).

The amounts of arsenic in plants observed at this site are generally orders of magnitude higher than has been observed in plants analysed elsewhere in New Zealand, even from soil with elevated arsenic (Lee et al., 1992; Longhurst, Roberts, & Waller, 2004). Ferns similar to the *Blechnum* sp studied here but growing on soil with <200 mg/kg As have only 2 mg/kg As (dry weight) (Lee et al., 1992). These As contents are considerably lower than those observed in hyperaccumulating ferns (Ma et al., 2001). Arsenic contents of *Juncus* reed species at a highly As-contaminated mine site in Australia (Ashley & Lottermoser, 1999) are only ca. 100 mg/kg, similar to those observed in this study. In contrast, Robinson et al. (2003) report up to 1,766 mg/kg (dry weight) As in water cress (*Lepidium sativum*) growing in river sediment with slightly elevated As content. Clearly, As uptake by plants is strongly species-dependent.

The moss species examined in this study were found to consistently absorb the highest amounts of arsenic (Tables I and II). This was expected from observations elsewhere (Ohnuki et al., 2002; Rasmussen & Anderson, 1999). In our study, the adventive species *H. coalitis* appears to be an important species for initial colonization of the HFO at Globe Hill. However, this species absorbed nearly 0.2 wt% As (Table I), thus maintaining elevated As in the surface biosphere during revegetation. The second adventive moss species analysed, *P. wahlenbergii*, from the

Prohibition wetland was even more effective at absorbing arsenic into its structure, with up to 3 wt% observed (Figure 5; Table II). Both collection periods confirmed very high As contents in above ground structures of *P. wahlenbergii*. *P. wahlenbergii* is clearly a hyperaccumulator in this setting, and thus has a negative effect on natural remediation processes. However, *P. wahlenbergii* grows only in the wettest part of the wetland, and will probably be superseded by species that absorb less arsenic (Figure 3; Table II) as the wetland is progressively filled in by sedimentation.

7 Conclusions

The three sites examined in this study have extremely high arsenic concentrations in substrates (up to 40 wt% As). Wetland waters, and presumably draining rainwater, also have strongly elevated arsenic concentrations (up to 77 mg/L As). These extremely arsenic-rich environments are being naturally revegetated on a 50-year time scale by colonization from nearby seed sources. In two of the sites examined, the high arsenic environment does not appear to be hindering revegetation. In the third site, revegetation may be being hindered only by low nutrient status, not high arsenic concentrations.

Native and adventive shrubs that are becoming established on these sites absorb little arsenic into their structures (<40 mg/kg), despite the high arsenic substrates in which they are growing. Likewise, some adventive grass and rush species have low or modest arsenic concentrations (typically <100 mg/kg), but there may be a seasonal effect on uptake levels that can periodically elevate As to higher concentrations. In contrast, ferns and mosses absorb higher amounts of arsenic, and in particular, *P. wahlenbergii* is apparently an arsenic hyperaccumulator, and As contents up to 3 wt% were observed. Hence, mosses can be a liability in this revegetation process, from a chemical point of view, as they continually transfer arsenic from the substrate to the biosphere. However, mosses can also act as important initiators of plant colonization by providing a physical substrate that is suitable for seed germination and establishment. Antimony was present in all analysed plants with the same As/Sb ratio as in the substrates (ca 1,000:1). Hence, antimony is only a minor component of the metalloid load at these sites.

Remediation of extremely arsenic-rich sites such as those described in this study could be done rapidly and cheaply by revegetating with species that absorb little arsenic, thereby essentially separating the substrates from the external environment. The most useful species identified in this study for this process are the shrubs *L. scoparium*, *F. excorticata*, *G. littoralis*, and *U. europaeus*. Dense establishment of these species, facilitated by addition of appropriate nutrients, could effectively and rapidly isolate arsenic-rich mine wastes. This process would not stop As-bearing leachate, but it would limit water penetration, and, more importantly, it would form a buffer between the arsenic-bearing material and surface biological activity, including casual human activity. We propose this approach for dealing with small, isolated, highly arsenic-contaminated sites in areas removed from human populations. Separate treatment of As-bearing leachates may be necessary as well.

Acknowledgments This research was funded by the University of Otago and CRL Energy Ltd. Tina Bayer collected some of the samples at Prohibition wetland site, and Annette King assisted with sample preparation. Discussions with Lucy Hewlett, John Taylor, and Nat Wilson helped our understanding of the mines of the area. Department of Conservation kindly provided logistical assistance with some of the sampling. Alan Fife assisted with moss identification and information. Comments from two anonymous reviewers improved the presentation of the manuscript.

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