

Trace Element Uptake by Mitchell Grasses Grown on Mine Wastes, Cannington Ag–Pb–Zn Mine, Australia: Implications for Mined Land Reclamation

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Abstract This study was conducted to determine the metal (Ag, Al, As, Cd, Co, Cu, Fe, Mn, Ni, Pb, Sb, Zn) tolerance and uptake of Mitchell grasses when grown on waste rocks and tailings of a base metal mine, Australia. The objective of conducting such phytoremediation studies was to gain data relating to the implementation and effectiveness of capping and revegetation strategies for mine waste repositories in regions of native grasslands. Pot trials demonstrate that Mitchell grasses are metal tolerant and have the ability to accumulate significant concentrations of metals (Pb, Zn) into their above-ground biomass. Concentrations of metals in Mitchell grasses were evaluated in terms of maximum allowable dietary levels in livestock. The pot trial project revealed that if Mitchell grasses were to be used for mined land reclamation and were grown on tailings, the grasses

could potentially accumulate large quantities of Zn in their tissue, potentially causing harmful effects on animals feeding on them. Hence, it is undesirable that Mitchell grasses are grown on and their root system come in contact with tailings with elevated level of Zn. Otherwise, the species may accumulate phyto- and zootoxic concentrations of Zn. The metal tolerance, the tendency to accumulate metals in the above-ground biomass and the significant root penetration depth of Mitchell grasses have implications for the design of tailings storage facilities. Capping of waste repositories, containing elevated metal concentrations and using a cover system without capillary breaks, clay layers or alternative strategies, may not be sustainable in the long term. The application of phosphate amendments to tailings may represent an alternative strategy to limit the uptake of metals by Mitchell grasses. The pot trials prove that the addition of phosphate to mine wastes decreases the bio-availability of metals in these materials and reduces the Pb and Zn concentration in Mitchell grasses growing on them. Thus, the addition of phosphate amendments to the top layers of metal-liferous mine wastes may represent an alternative waste management strategy.

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1 Introduction

At many mine sites, the construction of an effective and sustainable vegetation community generally represents an integral part of mine site rehabilitation. Only a vegetated or rock armoured landscape will lead to site stability, effectiveness of dry covers and minimisation of deleterious off-site effects (Mulligan 1998). Another important objective of rehabilitation includes the return of the mined land to a condition that allows a particular post-mining land use. Mining tenements, particularly those enclosed by pastoral leases, may be required to rehabilitate as much area as practicable of closed mine sites to a land use capability that would allow grazing (e.g. Bruce et al. 2003). In Australia, mining operations focus on the establishment of native plant species in their rehabilitation program or the establishment of pasture-based systems, using exotic tussock-forming grasses such as Rhodes grass (*Chloris gayana* Kunth cv. 'Pioneer'), Vetiver grass (*Vetiveria zizanioides*) and Buffel grass (*Cenchrus ciliaris*; e.g. Harwood et al. 1999; Prasad 2006). The characteristics and metal tolerance of Rhodes grass have been the subject of considerable research (e.g. Carroll et al. 2000; Keeling and Werren 2005). By comparison, the use of native grasses in the rehabilitation of metalliferous mine sites has been pursued with less vigour, despite the fact that many mining operations are required to use native grass species for mined land reclamation. The revegetation of metalliferous mine sites poses particular challenges as the vegetation at such sites may not only have to grow on substrates with poor nutrient status, high salinity and low pH but also the plants have to be tolerant to elevated metal concentrations as they colonise metalliferous soils and wastes (e.g. Grant et al. 2002; Schroeder et al. 2005).

This study was conducted to explore the use of native grasses for mined land rehabilitation at the Cannington Ag–Pb–Zn mine, Australia. Most importantly, the study sought to determine the metal tolerance and uptake of Mitchell grasses when grown through greenhouse pot trials on Cannington tailings and waste rocks containing variable amounts of phosphate fertilizer and locally available siltstone and limestone amendments. The objective of conducting such phytoremediation studies was to gain data relating to the implementation and effectiveness of capping and revegetation strategies for mine waste repositories.

Hence, this study contributes to improving rehabilitation efforts of base metal mine sites in regions of native grasslands.

2 Materials and Methods

2.1 Cannington Mine

The Cannington mine is located in northwest Queensland, Australia, approximately 200 km south-east of Mount Isa, at latitude 21°52'09" S, longitude 140°55'10" E. The mine lease is situated in the so-called Channel Country or Mitchell Grass Plains. The genus *Astrebla* (Mitchell Grass) includes Curley Mitchell (*Astrebla lappacea*), Bull Mitchell (*Astrebla squarrosa*), Hoop Mitchell (*Astrebla elymoides*) and Barley Mitchell (*Astrebla pectinata*) grass. These four species of Mitchell grass are long-lived perennial medium-sized deep-rooted tussock grasses. They represent important native open-range fodder grasses in the monsoonal tropics and occur in extensive areas on the clay-rich soils and cracking clay plains of northern Australia (Mallet and Orchard 2002). At Cannington, the Mitchell grasses largely grow on slightly alkaline (pH 7 to 8) vertosol soils. The Mitchell grasslands with their *Astrebla* and other grass species encompass 0.3 million km² of southeastern Queensland, the northern and central Northern Territory, the east Kimberley region of Western Australia and the northern regions of South Australia (Fig. 1).

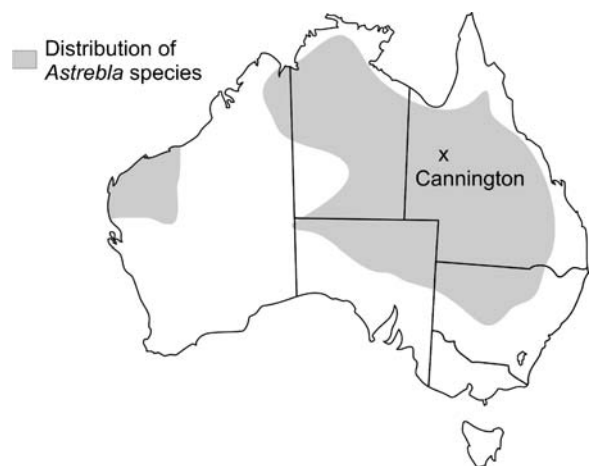


Fig. 1 Location of Cannington mine site and distribution of *Astrebla* species on the Australian continent (after Mallett and Orchard 2002)

The Cannington deposit represents a so-called Broken Hill-type Ag–Pb–Zn deposit, which is located within the Eastern Succession of the Proterozoic Mount Isa Inlier. The Cannington ore bodies are hosted by a sequence of migmatitic biotite–sillimanite–garnet bearing quartzofeldspathic gneisses, with minor amphibolites (Bodon 1998; Walters and Bailey 1998). The treated ores consist of major quartz, minor amounts of carbonate, chlorite, fluorite, garnet, magnetite, pyroxmangite and pyroxenes and traces of hornblende, apatite, biotite, epidote, feldspar, gahnite, graphite, ilvaite, montmorillonite, muscovite, olivine, pyrosmalite, sillimanite and talc (Table 1). The dominant sulphide minerals are sphalerite and galena. Trace sulphide minerals include arsenopyrite, chalcopyrite, freibergite, loellingite, marcasite, pyrrhotite,

pyrite, pyrrhotite and a series of Ag-sulphosalts and antimonides (Bodon 1998; Walters and Bailey 1998). Prior to mining, the deposit contained at least 43.8 Mt with 11.6% Pb, 4.4% Zn and 538 g/t Ag (Walters and Bailey 1998). Geochemical analyses also show elevated As, Cd, Cu, F and Sb concentrations in the mined ore lenses (Walters and Bailey 1998).

Since 1997, the Cannington process plant has employed grinding, flotation and filtration methods to produce a Zn concentrate, a Ag-rich Pb concentrate and a waste tailings stream. Various chemicals are used in the flotation circuit, particularly lime, sodium metabisulphide, xanthates, sulphuric acid and aluminium sulphate, which enter the tailings stream. As such, the pH of leachate effluent discharged to the tailings is often below 3, whereas the primary tailings have a natural to slightly basic pH. Tailings are either mixed with cement and backfilled into mined-out stopes or are deposited in the tailings storage facility.

Table 1 Mineralogy of Cannington ore (Walters and Bailey 1998; Bodon 1998) as well as tailings, waste rock, limestone and siltstone samples that were used for the growth experiments (major >10%; minor <10%; trace <1%)

Material	Mineralogy
Ore	Characteristic minerals: Ag-sulphosalts, antimonides, apatite, arsenopyrite, biotite, carbonate, chalcopyrite, chlorite, epidote, feldspar, fluorite, freibergite, gahnite, galena, garnet, graphite, hornblende, ilvaite, loellingite, magnetite, marcasite, montmorillonite, muscovite, olivine, pyrrhotite, pyrite, pyroxenes, pyroxmangite, pyrosmalite, quartz, sillimanite, sphalerite, talc
Tailings	Major: quartz Minor: amphibole, plagioclase Trace: anglesite, bassanite, biotite, brucite, calcite, chlorite, dolomite, fayalite, fluorite, galena, garnet, gypsum, halite, hedenbergite, hornblende, HFO phases, K-feldspar, laumontite, magnetite, native sulphur, natrojarosite, plumbojarosite, pyrite, sphalerite, szomolnokite, talc
Waste rock	Major: quartz Minor: amphibole, biotite, calcite, chlorite, dolomite, fayalite, garnet, hedenbergite, hornblende, K-feldspar, plagioclase, talc Trace: galena, pyrite, sphalerite
Limestone	Major: calcite, quartz Minor: amphibole, expanding clay, jarosite, kaolinite, K-feldspar, mica, plagioclase
Siltstone	Major: kaolinite, quartz Minor: muscovite/illite Trace: chlorite, magnetite, pyrite

2.2 Substrates

Tailings and waste rock samples were collected from the Cannington mine site. Waste rock samples (~50 kg) comprised random grab sample composites and were taken from traverses across waste rock stockpile faces. Tailings (~40 kg) were collected from shallow depths (0–200 mm) of cell 3 of the Cannington tailings storage facility and represent partially oxidised materials. Local limestone and siltstone samples (~40 kg) were taken from profile cuttings, approximately 4 and 7 km east of the current mining lease, respectively.

All solid rock samples were air-dried, whilst wet tailings were oven-dried at 60°C to limit sulphide oxidation. Limestone, siltstone and waste rock samples were crushed and sieved to less than 2 mm. Sample aliquots of tailings, waste rock, limestone and siltstone samples were ground in a chrome steel mill in preparation for chemical and X-ray diffraction (XRD) analysis. The growth experiments also used a commercial grade phosphate fertilizer (Trifos; Incitec Pivot Ltd.) as an amendment. Trifos is a granular, partially soluble (solubility 18 g L⁻¹; pH 3) triple superphosphate fertilizer, comprising Ca(H₂PO₄)₂ with subordinate CaNH₄HP₂O₇ and Ca(HPO₃H)₂, as shown by XRD studies. Limited pot trials used an MKP fertilizer (Incitec Pivot Ltd), a highly soluble phosphate fertilizer consisting of potassium dihydrogen orthophosphate.

2.3 Mineralogical and Geochemical Analyses

Sample powders of waste rocks, tailings, limestone and siltstone were dissolved in a hot HF–HNO₃–HCl–HClO₄ acid mixture and analysed by inductively coupled plasma mass spectrometry (ICPMS) for Ag, Al, As, Ca, Cd, Co, Cu, Fe, K, Mg, Mn, Mo, Ni, P, Pb, S, Sb and Zn at Australian Laboratory Services (ALS), Brisbane, Australia. Duplicate samples and an aliquot of the geochemical reference material GXR-2 were submitted for data quality control and assurance. The obtained GXR-2 concentrations corresponded closely to the published compilation concentrations. Standard deviation values for the repeated analysis of the reference material were below 5% of the mean concentrations for each element, indicating high accuracy of the results. Sulphate sulphur was analysed using a dilute calcium phosphate extract of sample powders followed by inductively coupled plasma atomic emission spectrometry (ALS, Brisbane, Australia). The sulphide sulphur content of samples was assumed to represent the maximum potential acidity (MPA) of samples which was calculated by difference between the total and sulphate sulphur value. The acid neutralising capacity (ANC) of tailings and waste rocks was determined by titration (ALS, Brisbane, Australia). The difference between MPA and ANC yielded the net acid producing potential (NAPP). Paste and net acid generation (NAG) pH measurements were performed on waste rocks and tailings following the procedure by Morin and Hutt (1997). Such pH measurements provide a preliminary evaluation of the wastes' acid generation potential. Mineral identification of rock and waste samples was performed at the James Cook University Advanced Analytical Centre (JCU AAC) using XRD and quantitative computational software (SIROQUANT, EVA).

2.4 Growth Experiments

All growth experiments were conducted in a shade house at James Cook University, Cairns, Australia. The climate is humid tropical, with mean temperatures ranging from a June mean minimum (17°C) to a January mean maximum temperature (31°C).

The plant growth media consisted of waste rocks and tailings, amended with variable proportions of

limestone, siltstone and phosphate fertilizer. Substrate materials were mixed at varying weight proportions. The substrate mixtures were loaded into 280 ml plant propagation pots. Sample aliquots of the substrate mixtures were collected for partial extraction analyses. Seedlings of Barley, Bull and Curley Mitchell grass seeds were obtained from a commercial supplier (Nindethana Seed Service, Albany, Australia), and ten seeds were buried directly into the top 1 cm of the substrate layer of each pot. The pots had a small amount of Osmocote N–P–K fertilizer added (~1 g) to stimulate plant growth. Pots were watered to field capacity every second day. Four to five replicates of each substrate and grass species were prepared for cultivation. After 1 to 3 weeks, any seeds that did not germinate were replaced with fresh seeds. Pots were re-arranged to randomise growth effects inside the shade house. After 8 to 10 weeks, all above-ground biomass was harvested, rinsed with MilliQ water and oven-dried at 30°C for 1 week before the dry weight was recorded. The resulting biomass was digested using a HNO₃–H₂O₂ microwave digestion technique, and samples ($n=106$) were analysed by ICPMS (Ag, Al, As, Cd, Co, Cu, Fe, Mn, Ni, Pb, Sb, Zn) at the JCU AAC.

2.5 Partial Extraction

The bio-availability of trace elements in substrates can be evaluated using extraction techniques such as diethylene triamine pentaacetic acid (DTPA) and ethylenediaminetetraacetic acid (EDTA; e.g. Burgos et al. 2008). Selected elements were extracted from all plant growth media ($n=106$) using the DTPA–CaCl₂–triethanolamine (TEA)–HCl extraction procedure described by Rayment and Higginson (1992). The studied substrates also underwent a partial extraction procedure using the EDTA–NH₄HCO₃ bio-available reagent (Rayment and Higginson 1992). The procedure aimed to compare the results of this technique with those of the DTPA extraction. The DTPA–CaCl₂–TEA–HCl and EDTA–NH₄HCO₃ extracts were subsequently analysed for Ag, Al, As, Cd, Co, Cu, Fe, Mn, Ni, Pb, Sb and Zn using ICPMS techniques (JCU AAC). The analyses of sample replicates were largely consistent, indicating strong precision of the results. The pH values of the substrates ($n=106$) were measured in distilled water at a soil/solution ratio of 1:5.

3 Results

3.1 Substrate Characterisation

3.1.1 Tailings and Waste Rocks

The Cannington tailings have major (i.e. >1 wt.%) concentrations of Al, Ca, Fe, S_{total} and S_{sulphide} , minor (i.e. >100 ppm) As, Cu, K, Mg, Mn, Na, P, Pb, S_{sulphate} , Sb and Zn and traces (i.e. <100 ppm) of Ag, Cd, Co, Mo and Ni (Table 2). By comparison, the tested waste rocks tend to possess higher major and lower trace element contents (with the exception of

Co, Cu, Mn, Ni, P, Pb, S and Zn; Table 2). The element distributions are consistent with the occurrence of relatively abundant primary aluminosilicates (i.e. K-feldspar, plagioclase, chlorite, talc, biotite, garnet, amphibole, hedenbergite, hornblende, fayalite), magnetite, calcite, dolomite, fluorite, brucite, laumontite and secondary minerals (particularly in tailings; i.e. gypsum, bassanite, plumbojarosite, natrojarosite, anglesite, halite, szomolnokite, native sulphur) as indicated by XRD and petrographic studies (Table 1). The presence of sulphides (i.e. pyrite, pyrrhotite, sphalerite and galena) is evident in XRD traces and supported by the known mineralogy of

Table 2 Geochemistry (mean total element concentrations) and static test data of tailings, waste rock, limestone and siltstone samples that were used for the growth experiments

	Tailings (n=5)	Waste rocks (n=5)	Limestone (n=5)	Siltstone (n=5)
Major elements (wt.%)				
Al	1.27	6.45	4.74	10.92
Ca	4.29	4.33	12.6	0.05
Fe _{total}	7.74	8.17	3.34	1.09
K	0.45	1.57	0.78	0.66
Mg	0.95	1.77	0.56	0.10
Mn	0.90	0.39	0.16	<0.01
Na	0.27	1.39	0.19	0.09
P	0.28	0.11	0.15	0.06
Pb	0.85	0.70		
S _{total}	1.52	0.97	0.23	0.03
S _{sulphate}	0.34	0.23	0.18	<0.01
S _{sulphide}	1.18	0.74	0.05	0.02
Zn	0.49	0.37		
Trace elements (ppm)				
Ag	41.9	33.2	0.3	0.10
As	626	385	33.4	3.8
Cd	25.1	15.6	5.3	0.02
Co	17.4	34.6	19.1	1.03
Cu	76.4	248	64.3	8.2
Mo	3.0	1.5	85.5	0.85
Ni	8.2	22.1	109	3.37
Pb			21.4	15.7
Sb	136	63.3	6.7	0.36
Zn			313	10.3
Static test data				
Paste pH	6.92	6.78	7.77	4.73
NAG pH	4.38	6.36	9.36	4.21
ANC (kg H ₂ SO ₄ /t)	34.3	36.3	na	na
MPA (kg H ₂ SO ₄ /t)	36.1	27.6	na	na
NAPP (kg H ₂ SO ₄ /t)	+1.8	-13.7	na	na

na not analysed

processed ores and the abundance of S_{sulphide} , Pb and Zn in the analysed tailings and waste rocks (Table 2). Powder XRD analyses of oxidised tailings did not reveal any crystalline Fe oxide or hydroxide phases. Hence, oxidised red-brown coloured tailings are impregnated by non-crystalline hydrous ferric oxide (HFO) phases.

Paste and NAG pH measurements of milled tailings confirm that the wastes are acid producing as they have a mean paste and NAG pH value of 6.92 and 4.38, respectively (Table 2). Also, the tailings have an elevated S_{sulphide} content of 1.18 wt.%. Hence, the oxidation and wetting of tailings lead to the oxidation of sulphides, release of sorbed hydrogen and metal ions, the hydrolysis of iron and associated acid production and the dissolution of acid producing mineral efflorescences (e.g. szomolnokite). Thus, the investigated Cannington tailings have a minor NAPP (Table 2). By comparison, the tested waste rocks have a lower S_{sulphide} content and hence a lower MPA value. As a result, the waste rocks tested can be classified as non-acid generating (Table 2).

3.1.2 Limestone and Siltstone

The limestone displays major (i.e. >1 wt.%) concentrations of Al, Ca and Fe, minor (i.e. >100 ppm) K, Mg, Mn, Na, Ni, P, S_{sulphide} and Zn and traces (i.e. <100 ppm) of Ag, As, Cd, Co, Cu, Mo, Pb and Sb (Table 2). Such element distributions are consistent with the occurrence of relatively abundant carbonate and silicate minerals (Table 1). The rocks are composed of major quartz and calcite and minor amounts of amphibole, expanding clay, kaolinite, K-feldspar, mica, plagioclase and jarosite. The presence of jarosite reflects the oxidation of metal sulphides, and the limestone exhibits distinctly elevated metal and metalloid values. Compared to the average geochemistry of limestones (Berkman 2001), there is a moderate to strong enrichment of As (10 \times), Cd (50 \times), Co (3 \times), Cu (4 \times), Mo (85 \times), Ni (13 \times), Pb (2.5 \times) and Zn (12 \times ; Table 2). Alkaline paste and NAG pH values highlight the fact that this mineralised limestone is still an acid consuming rock material.

The siltstone contains major Al and Fe values, minor contents of Ca, K, Mg, Na, P and S_{sulphide} and traces of Ag, As, Cd, Co, Cu, Mo, Ni, Pb, Sb and Zn (Table 2). The rock is composed of major quartz and kaolinite as well as minor muscovite/illite and

traces of chlorite, magnetite and pyrite (Table 1). In the absence of carbonates, the low S_{sulphide} value (0.02 wt.%) due to pyrite is still high enough to cause distinctly acid paste and NAG pH values (Table 2).

3.2 Partial Extraction of Substrates

pH measurements of substrate mixtures demonstrate that the siltstone, waste rocks and tailings are acidic, compared to the mildly alkaline limestone-amended waste rocks and tailings (Tables 2, 3 and 4). The slightly acidic pH value of siltstone-amended waste rocks and tailings (pH 5.6–6.3) is likely due to the oxidation of trace pyrite. Also, the addition of the Trifos fertilizer led to a distinct decrease in the pH of phosphate-amended tailings and waste rocks.

All substrate mixtures used for the trials were subject to leaching experiments using DTPA and EDTA in order to simulate the phytoavailability of metals and metalloids. Substrate mixtures that exhibited high total metal concentrations displayed comparatively high EDTA extractable metal values (Table 3). That is, tailings and waste rocks as well as limestones and siltstones containing proportions of tailings or waste rocks have elevated extractable As, Cd, Co, Fe, Mn, Pb, Sb and Zn concentrations (Table 3). Extraction concentrations of Pb and Zn are significantly higher than those of the other elements. The concentrations for Ag and Al from the leach solutions were generally below the limit of detection. There are generally higher solubilities of the analysed elements in substrates containing tailings or waste rocks. By comparison, the siltstone substrate exhibits the highest bio-available Al and the lowest bio-available concentrations of As, Cd, Cu, Fe, Ni, Pb, Sb and Zn. The distinctly elevated concentration of EDTA extractable Al in siltstone substrates is likely due to sulphide oxidation and associated acid leaching of aluminosilicates. The addition of siltstone to tailings or waste rocks leads to a pronounced decrease in substrate pH and associated increased dissolution of sulphides and higher solubilities of metals and metalloids (Table 3).

The proportion of each metal extracted by the EDTA solution was calculated relative to its total content in the substrate mixtures. Results indicate generally low proportional solubilities for Al and Fe (<0.1%), medium proportional solubilities for As, Co, Cu, Mn, Ni, Sb and Zn (1–10%) and elevated

Table 3 Average pH and EDTA extractable element concentrations (ppm) in substrate mixtures used for the plant growth experiments

Substrate	pH	Ag	Al	As	Cd	Co	Cu	Fe	Mn	Ni	Pb	Sb	Zn
100% limestone (<i>n</i> =3)	7.8	<0.002	<0.1	0.6	0.13	0.07	6.9	3.9	4.9	0.89	11.9	0.06	3.6
85% limestone + 15% tailings (<i>n</i> =3)	7.7	<0.002	<0.1	4.6	0.71	0.11	6.5	9.9	8.7	1.06	234	0.51	80.3
75% limestone + 25% tailings (<i>n</i> =3)	7.8	<0.002	<0.1	6.4	0.91	0.12	6.2	11.1	9.5	0.98	317	0.79	109
50% limestone + 50% tailings (<i>n</i> =3)	7.8	<0.002	<0.1	21	1.7	0.25	7.8	18.8	9.6	0.74	664	2.6	218
85% limestone + 15% waste rocks (<i>n</i> =3)	7.8	<0.002	<0.1	1.2	0.39	0.05	6.3	9.8	5.1	0.68	132	0.37	39.9
75% limestone + 25% waste rocks (<i>n</i> =3)	7.8	<0.002	<0.1	1.5	0.54	0.09	7.0	11.2	6.6	0.86	234	0.54	55.6
50% limestone + 50% waste rocks (<i>n</i> =3)	7.9	<0.002	<0.1	2.4	0.76	0.11	5.9	14.8	5.8	0.59	527	1.1	83.2
100% siltstone (<i>n</i> =1)	4.7	<0.002	33.5	0.29	0.03	0.09	1.3	69.5	5.8	0.13	8.6	0.03	2.6
100% siltstone + 10 g Trifos (<i>n</i> =8)	4.7	<0.002	7.2	0.06	0.04	0.16	1.1	38.5	4.4	0.45	1.2	0.06	<2
85% siltstone + 15% tailings (<i>n</i> =2)	5.6	<0.002	0.24	6.1	0.54	0.49	0.94	34.3	65.9	0.21	331	0.50	57.0
75% siltstone + 25% tailings (<i>n</i> =2)	5.8	<0.002	<0.1	10.6	1.00	0.63	1.3	25.6	81.8	0.27	639	0.88	110
50% siltstone + 50% tailings (<i>n</i> =2)	6.2	<0.002	<0.1	22.8	2.08	0.75	2.4	24.5	76.2	0.30	697	2.5	208
85% siltstone + 15% waste rocks (<i>n</i> =2)	5.7	<0.002	0.70	3.7	0.38	0.33	1.7	43.4	20.8	0.20	282	0.85	40.0
75% siltstone + 25% waste rocks (<i>n</i> =2)	6.1	<0.002	0.24	3.3	0.45	0.25	1.9	35.8	18.8	0.16	362	1.2	40.8
50% siltstone + 50% waste rocks (<i>n</i> =2)	6.3	<0.002	0.23	2.3	0.60	0.18	3.1	30.4	11.6	0.12	560	1.5	63.9
100% tailings (<i>n</i> =1)	6.9	0.002	2.4	47.5	2.85	1.11	3.9	13.2	2.7	0.57	234	1.7	437
100% tailings + 5 g Trifos (<i>n</i> =3)	6.1	<0.002	0.67	6.1	2.5	1.1	1.5	75.5	111	0.72	326	2.3	208
100% tailings + 10 g Trifos (<i>n</i> =8)	6.1	<0.002	1.3	4.2	0.82	0.48	1.7	52.7	86.1	0.33	300	1.7	117
100% waste rock (<i>n</i> =1)	6.7	<0.002	<0.1	7.7	1.1	0.39	4.2	59.4	7.5	0.15	543	1.37	121
100% waste rocks + 5 g Trifos (<i>n</i> =3)	6.7	<0.002	1.6	1.9	0.67	0.25	2.9	58.2	27.5	0.25	298	1.4	110
100% waste rock + 10 g Trifos (<i>n</i> =8)	6.4	<0.002	1.5	1.5	0.37	0.21	2.0	47.6	29.9	0.17	143	0.89	59.1
100% limestone + 5 g Trifos (<i>n</i> =3)	7.5	<0.002	0.87	0.57	0.19	0.07	6.2	11.6	7.8	1.2	4.24	0.05	2.6
85% limestone + 15% tailings + 5 g Trifos (<i>n</i> =3)	7.5	<0.002	0.30	3.4	0.45	0.09	5.3	9.7	10.9	1.3	126	0.38	44.9
75% limestone + 25% tailings + 5 g Trifos (<i>n</i> =3)	7.5	<0.002	0.35	4.4	0.58	0.12	5.1	13.6	13.8	1.4	173	0.62	62.7
50% limestone + 50% tailings + 5 g Trifos (<i>n</i> =3)	7.4	<0.002	0.31	5.7	0.98	0.21	5.6	25.8	25.4	1.3	313	1.2	126
25% limestone + 75% tailings + 5 g Trifos (<i>n</i> =3)	6.9	<0.002	0.76	4.6	1.9	0.53	5.7	30.4	68.5	1.2	346	1.5	243
85% limestone + 15% waste rocks + 5 g Trifos (<i>n</i> =3)	7.7	<0.002	0.36	1.3	0.27	0.08	6.3	10.5	8.55	1.2	82.6	0.34	22.0
75% limestone + 25% waste rocks + 5 g Trifos (<i>n</i> =3)	7.8	<0.002	0.24	1.4	0.32	0.07	6.1	10.9	8.15	1.1	108	0.43	32.1
50% limestone + 50% waste rocks + 5 g Trifos (<i>n</i> =3)	7.6	<0.002	0.86	2.1	0.41	0.09	5.6	26.0	9.68	0.88	251	0.90	59.3
25% limestone + 75% waste rocks + 5 g Trifos (<i>n</i> =3)	7.2	<0.002	0.87	2.0	0.44	0.12	4.3	34.1	16.1	0.69	225	1.1	68.2

n number of substrates analysed

proportional solubilities for Cd and Pb (>10%). The low proportional solubilities of Al and Fe probably reflect the fact that these two elements remain in insoluble form as residual silicate and oxide minerals. The average proportions as well as absolute EDTA extractable concentrations of As, Cd, Co, Mn, Pb, Sb and Zn are substantially higher in the mineralised

substrates than in the pure limestone and siltstone, reflecting a higher proportion of leachable As, Cd, Co, Mn, Pb, Sb and Zn bearing minerals (i.e. sulphides) in the waste-amended substrates.

The application of DTPA to the substrates resulted in distinctly lower As, slightly less Al, Cd, Co, Cu, Fe, Pb and Sb concentrations and similar extractable Mn and

Table 4 Average pH and DTPA extractable element concentrations (ppm) in substrate mixtures used for the plant growth experiments

Substrate	pH	Ag	Al	As	Cd	Co	Cu	Fe	Mn	Ni	Pb	Sb	Zn
100% limestone (<i>n</i> =3)	7.8	<0.002	<0.2	0.05	0.11	0.06	3.0	1.0	4.4	0.77	2.9	0.01	1.9
85% limestone + 15% tailings (<i>n</i> =3)	7.7	<0.002	<0.2	0.11	0.88	0.09	3.5	2.7	7.8	0.93	85.7	0.03	85.4
75% limestone + 25% tailings (<i>n</i> =3)	7.8	<0.002	<0.2	0.11	1.28	0.09	3.4	3.3	9.1	0.94	112	0.04	127
50% limestone + 50% tailings (<i>n</i> =3)	7.8	<0.002	<0.2	0.14	2.3	0.14	4.3	5.9	8.6	0.61	224	0.12	215
85% limestone + 15% waste rocks (<i>n</i> =3)	7.8	<0.002	<0.2	0.07	0.40	0.04	3.2	1.6	4.2	0.59	38.7	0.02	38.1
75% limestone + 25% waste rocks (<i>n</i> =3)	7.8	<0.002	<0.2	0.07	0.62	0.09	3.7	2.3	5.8	0.78	67.6	0.03	57.4
50% limestone + 50% waste rocks (<i>n</i> =3)	7.9	<0.002	<0.2	0.06	0.85	0.09	3.6	3.4	5.2	0.53	304	0.07	83.1
100% siltstone (<i>n</i> =1)	4.7	<0.002	2.5	0.02	0.02	0.09	0.56	18.8	3.8	0.12	4.7	0.01	1.66
100% siltstone + 10 g Trifos (<i>n</i> =8)	4.7	<0.002	2.5	0.02	0.03	0.12	0.93	8.7	3.9	0.41	0.67	0.01	1.03
85% siltstone + 15% tailings (<i>n</i> =2)	5.6	<0.002	<0.2	0.23	0.51	0.61	0.61	21.8	83.4	0.22	391	0.04	58.4
75% siltstone + 25% tailings (<i>n</i> =2)	5.8	<0.002	<0.2	0.26	0.92	0.72	0.97	14.2	122	0.26	591	0.08	100
50% siltstone + 50% tailings (<i>n</i> =2)	6.2	<0.002	<0.2	0.18	2.1	0.68	1.1	3.3	146	0.21	219	0.12	152
85% siltstone + 15% waste rocks (<i>n</i> =2)	5.7	<0.002	<0.2	0.24	0.26	0.32	0.74	14.7	18.9	0.16	159	0.05	28.8
75% siltstone + 25% waste rocks (<i>n</i> =2)	6.1	<0.002	<0.2	0.32	0.36	0.27	1.1	9.7	21.5	0.14	364	0.10	34.7
50% siltstone + 50% waste rocks (<i>n</i> =2)	6.3	<0.002	<0.2	0.17	0.45	0.14	1.4	5.6	11.7	0.09	522	0.13	48.1
100% tailings (<i>n</i> =1)	6.9	0.001	0.1	0.27	2.3	0.34	1.51	5.1	1.5	0.07	110	0.12	218
100% tailings + 5 g Trifos (<i>n</i> =3)	6.1	<0.002	<0.2	1.1	3.6	1.2	0.53	20.2	142	0.82	201	0.32	187
100% tailings + 10 g Trifos (<i>n</i> =8)	6.1	<0.002	<0.2	0.82	0.58	0.41	0.48	11.8	96.1	0.27	121	0.15	77.6
100% waste rocks (<i>n</i> =1)	6.7	<0.002	0.1	0.43	0.55	0.21	1.2	18.4	3.5	0.04	167	0.21	34.2
100% waste rocks + 5 g Trifos (<i>n</i> =3)	6.7	<0.002	<0.2	0.38	0.38	0.17	1.1	5.2	18.3	0.21	91.1	0.09	46.5
100% waste rock + 10 g Trifos (<i>n</i> =8)	6.4	<0.002	<0.2	0.42	0.17	0.16	0.65	5.6	23.3	0.12	38.5	0.05	22.7
100% limestone + 5 g Trifos (<i>n</i> =3)	7.5	<0.002	<0.2	0.04	0.14	0.06	3.2	1.5	7.9	1.0	2.1	0.01	1.8
85% limestone + 15% tailings + 5 g Trifos (<i>n</i> =3)	7.5	<0.002	<0.2	0.11	0.47	0.08	2.8	2.5	10.9	1.2	48.4	0.01	48.2
75% limestone + 25% tailings + 5 g Trifos (<i>n</i> =3)	7.5	<0.002	<0.2	0.19	0.67	0.11	2.8	3.4	13.9	1.4	77.6	0.02	68.6
50% limestone + 50% tailings + 5 g Trifos (<i>n</i> =3)	7.4	<0.002	<0.2	0.35	1.1	0.17	3.2	4.9	23.7	1.4	157	0.06	109
25% limestone + 75% tailings + 5 g Trifos (<i>n</i> =3)	6.9	<0.002	<0.2	0.62	1.9	0.51	3.2	5.9	66.8	1.2	185	0.12	168
85% limestone + 15% waste rocks + 5 g Trifos (<i>n</i> =3)	7.7	<0.002	<0.2	0.06	0.19	0.06	2.6	2.4	7.5	1.1	38.1	0.01	16.2
75% limestone + 25% waste rocks + 5 g Trifos (<i>n</i> =3)	7.8	<0.002	<0.2	0.07	0.29	0.06	2.9	2.5	6.9	0.96	49.7	0.01	29.3
50% limestone + 50% waste rocks + 5 g Trifos (<i>n</i> =3)	7.6	<0.002	<0.2	0.14	0.39	0.07	3.1	4.2	8.7	0.88	102	0.03	47.7
25% limestone + 75% waste rocks + 5 g Trifos (<i>n</i> =3)	7.2	<0.002	<0.2	0.23	0.36	0.11	2.3	4.7	13.2	0.66	116	0.07	41.6

n number of substrates analysed

Zn values compared to those recorded in the EDTA extracts (Table 4). Both extraction techniques report similar element trends and relative element abundances, with a pronounced bio-availability of Pb and Zn compared to the other elements (Al, As, Cd, Co, Cu, Fe, Sb).

Substrate mixtures used for the trials were also amended with phosphate fertilizer (Tables 3 and 4).

The addition of phosphate fertilizers to mine wastes is known to reduce the solubility of metals due to the formation of insoluble or poorly soluble metal phosphate phases (Harris and Lottermoser 2006a, b). In this study, the addition of super-phosphate (i.e. 5 and 10 g Trifos) to tailings and waste rocks resulted in distinctly lower bio-available Cd, Cu, Pb and Zn

concentrations, when compared to tailings and waste rocks containing no super-phosphate (Tables 3 and 4). Also, bio-available concentrations of Cd, Pb and Zn in the limestone and phosphate-amended tailings and waste rocks were generally reduced by half, when compared to those substrate mixtures containing no super-phosphate. Thus, the addition of phosphate fertilizer drastically decreased the amount of phytoavailable Cd, Pb and Zn.

3.3 Plant Growth

Plant growth in terms of average plant height and biomass production was determined for all pot trials. There was no significant difference in growth between the three Mitchell grass species. The Mitchell grasses endured the range of tailings and waste rock mixtures, indicating that the species are highly tolerant to the elevated concentrations of metals and metalloids in the plant-growth media. Plant height and biomass production of all Mitchell grasses were particularly elevated when grasses were cultivated on (a) substrates with 100% limestone and 5 g Trifos fertilizer, (b) substrates with 25% to 85% limestone and 15% to 75% tailings or waste rocks and 5 g Trifos fertilizer and (c) 100% tailings and waste rocks amended with 10 g Trifos fertilizer. By contrast, pot trials using 100% tailings and waste rocks amended with 20 g Trifos and 20 g MKP fertilizer did not result in plant growth (Tables 5, 6 and 7), suggesting that an excessive application of fertilizer reduced substrate pH to a level that impacted on plant growth. Moreover, the acid pH of the siltstone substrate was detrimental to the growth of Mitchell grasses. Pure siltstone and phosphate-amended siltstone substrates displayed no plant growth, whilst siltstones mixed with 15% tailings or waste rocks showed limited plant growth and low biomass for all Mitchell grasses. Plant growth increased with decreased siltstone and increased (25% to 75%) tailings or waste rock proportions. Hence, near-neutral to slightly alkaline pH conditions are required for the successful germination, growth and survival of Mitchell grasses.

3.4 Uptake of Metals

Mitchell grasses growing on the various substrates accumulated a range of element contents (Tables 5, 6 and 7). The foliage of the Curley, Barley and Bull

Mitchell grasses displays similar metal distributions (i.e. $Mn > Zn > Cu > Ni > Pb > As > Cd > Co > Sb$), implying that the three different Mitchell grass species possess similar preferences for metal uptake and exclusion. The grass species display a general pattern of greater uptake of Mn and Zn and lesser uptake of Cu, Ni, Pb, As, Cd, Co and Sb in their tissue when growing in relatively unmineralised limestone or soil (Tables 5, 6 and 7).

However, the Mitchell grasses behave differently once metal levels in the substrate increase. A comparison between the foliage of Mitchell grasses growing on “background” limestone or soil substrates versus substrates containing tailings or waste rocks shows that the grasses exhibit a pronounced uptake of Pb and Zn into their above-ground biomass on metalliferous substrates (Tables 5, 6 and 7). The above-ground biomass of Curley, Barley and Bull Mitchell grasses has mean Pb and Zn concentrations that exceed those from the “background” soil and limestone substrates by one to two orders of magnitude. By contrast, the grasses display a much more subdued As, Cd and Co enrichment compared to Pb and Zn whilst there has been no significant change in the Cu and Ni values. Maximum accumulations of Pb in Curley and Barley Mitchell grasses occurred on slightly acidic metal-rich substrates (i.e. siltstone plus tailings or waste rocks; Tables 6 and 7). The highest concentrations of Zn were found in Curley, Bull and Barley Mitchell grasses growing in tailings and limestone-amended tailings. These substrates also display the highest bio-available concentrations of Pb and Zn (Tables 3 and 4).

Germination, growth and survival of plants are difficult to achieve in low-nutrient substrates such as tailings and waste rocks. In this study, all substrates, particularly the tailings, possess elevated phosphate concentrations (Table 2). These phosphate levels plus small amounts of Osmocote and the addition of the super-phosphate Trifos allowed plant growth in most investigated substrates (Tables 5, 6 and 7). Whilst the addition of 5 g super-phosphate to substrates reduced the bio-availability of Pb and Zn in tailings and waste rocks (Tables 3 and 4), it also resulted in lower metal concentrations in plant shoots (Tables 5, 6 and 7). Mitchell grasses growing on phosphate-amended substrates acquired much lower metal concentrations compared to grasses growing in non-amended substrates (Tables 5, 6 and 7). Yet, previous studies have

Table 5 Trace element concentrations (mg/kg in dry matter) in shoots of Bull Mitchell grass, grown in various substrates

Substrate	pH	Ag	Al	As	Cd	Co	Cu	Fe	Mn	Ni	Pb	Sb	Zn
100% soil (<i>n</i> =1)	na	0.04	na	<0.01	0.11	na	2.74	na	na	na	3.31	0.02	5.0
100% limestone (<i>n</i> =4)	7.71	<0.05	24.9	<1	0.32	<0.1	6.97	<100	47.4	2.36	2.13	<0.05	21.2
85% limestone + 15% tailings (<i>n</i> =4)	7.75	<0.05	44.9	1.2	1.08	<0.1	6.32	<100	80.8	2.60	4.69	<0.05	194
75% limestone + 25% tailings (<i>n</i> =4)	7.85	<0.05	34.1	1.29	1.76	<0.1	7.50	<100	112	3.40	4.52	<0.05	259
50% limestone + 50% tailings (<i>n</i> =2)	7.86	<0.05	38.9	1.22	2.87	0.17	7.02	<100	122	2.52	15.4	0.13	327
85% limestone + 15% waste rocks (<i>n</i> =4)	7.80	<0.05	22.3	1.03	0.58	<0.1	6.0	<100	35.6	1.46	2.38	<0.05	70.6
75% limestone + 25% waste rocks (<i>n</i> =4)	7.83	<0.05	26.6	<1	0.64	<0.1	7.33	<100	35.3	1.94	2.95	<0.05	111
50% limestone + 50% waste rocks (<i>n</i> =4)	7.90	<0.05	31.0	<1	1.19	<0.1	8.23	<100	54.1	2.14	6.89	<0.05	169
100% limestone + 5 g Trifos (<i>n</i> =4)	7.57	<0.05	8.54	1.11	0.30	0.11	7.21	<100	56.1	2.5	0.65	<0.05	15.5
85% limestone + 15% tailings + 5 g Trifos (<i>n</i> =4)	7.37	<0.05	7.15	<1	0.73	<0.1	6.33	<100	61.6	2.18	0.86	<0.05	157
75% limestone + 25% tailings + 5 g Trifos (<i>n</i> =3)	7.53	<0.05	9.56	<1	1.26	<0.1	6.41	<100	108	2.21	1.44	<0.05	211
50% limestone + 50% tailings + 5 g Trifos (<i>n</i> =4)	7.40	<0.05	11.6	1.63	1.72	0.21	8.06	<100	152	3.92	2.76	<0.05	284
25% limestone + 75% tailings + 5 g Trifos (<i>n</i> =4)	6.62	<0.05	6.05	2.52	4.02	0.63	6.74	<100	261	2.93	5.96	0.05	380
100% tailings + 5 g Trifos (<i>n</i> =3)	6.12	<0.05	9.69	4.20	4.22	4.75	6.19	<100	603	2.22	12.3	0.14	571
100% waste rocks + 5 g Trifos (<i>n</i> =3)	6.70	<0.05	4.09	3.32	0.78	1.14	6.91	<100	187	2.74	2.30	0.37	76.5
100% tailings + 20 g Trifos + 20 g MKP (<i>n</i> =0): no growth	5.54												
100% waste rocks + 20 g Trifos + 20 g MKP (<i>n</i> =0): no growth	5.53												
85% limestone + 15% waste rocks + 5 g Trifos (<i>n</i> =4)	7.68	<0.05	8.37	<1	0.43	<0.1	4.24	<100	27.9	0.79	1.07	0.05	42.9
75% limestone + 25% waste rocks + 5 g Trifos (<i>n</i> =4)	7.70	<0.05	5.16	<1	0.49	<0.1	4.11	<100	27.6	0.79	1.07	<0.05	51.4
50% limestone + 50% waste rocks + 5 g Trifos (<i>n</i> =4)	7.55	<0.05	5.20	1.06	0.84	<0.1	5.48	<100	79.0	1.10	2.67	<0.05	87.2
25% limestone + 75% waste rocks + 5 g Trifos (<i>n</i> =3)	7.33	<0.05	5.40	1.52	0.85	<0.1	4.78	<100	99.3	1.35	3.97	0.07	63.0

The chemistry of Bull Mitchell grass from an unmineralised background soil site, collected 7 km from the mine lease, is also shown (Gilfedder and Lottermoser 2008)

n number of pots with samples composited

established that phosphate addition to tailings can mobilise As into plants (e.g. Mains et al. 2006). In this study, the addition of 10-g Trifos to tailings and waste rocks led to increasing As concentrations in Curley and Barley Mitchell grass (Tables 5 and 7). The increased uptake of As is most likely due to the fact that arsenate and phosphate possess a similar competitive chemical behaviour in oxidising environments. Thus, whilst the addition of super-phosphate reduced the uptake of metals, the phosphate amendment also promoted As uptake by Mitchell grasses.

4 Discussion

4.1 Nature of Metal Uptake

The composition of plants reflects the availability of elements in the root area and the ability of the plant to absorb, transport and accumulate the elements. Plants tolerant to high concentrations of metals respond by exclusion, indication or accumulation of metals (Baker 1981). Excluders are plants that restrict the transport of metals to the shoots and maintain relatively low metal concentrations in the shoots over

Table 6 Trace element concentrations (mg/kg in dry matter) in shoots of Curley Mitchell grass, growing in various substrates

Substrate	pH	Ag	Al	As	Cd	Co	Cu	Fe	Mn	Ni	Pb	Sb	Zn
100% limestone (<i>n</i> =5)	7.92	<0.05	143	2.14	1.46	0.31	11.6	214	32.3	4.19	1.34	<0.05	22.3
85% limestone + 15% tailings (<i>n</i> =5)	7.65	0.06	78.4	2.88	4.72	0.25	11.1	185	59.1	4.56	8.75	0.26	360
75% limestone + 25% tailings (<i>n</i> =5)	7.87	0.06	60.9	2.83	3.70	0.11	9.25	174	77.6	3.34	10.9	0.17	351
50% limestone + 50% tailings (<i>n</i> =5)	7.91	<0.05	24.6	1.49	5.26	0.15	8.98	102	122	3.04	16.3	0.16	567
85% limestone + 15% waste rocks (<i>n</i> =5)	7.82	<0.05	84.1	3.99	1.85	0.31	11.6	144	37.5	2.64	3.65	0.15	120
75% limestone + 25% waste rocks (<i>n</i> =5)	7.85	0.05	151	2.03	2.28	0.38	11.2	243	24.6	2.41	9.56	0.26	134
50% limestone + 50% waste rocks (<i>n</i> =5)	7.88	0.06	112	2.74	3.35	1.09	14.3	240	68.3	6.03	40.1	0.75	238
100% siltstone (<i>n</i> =0): no growth	4.74												
100% siltstone + 10 g Trifos (<i>n</i> =0): no growth	4.70												
85% siltstone + 15% tailings (<i>n</i> =2)	5.62	<0.05	71.2	5.52	4.82	1.37	1.75	<100	617	0.49	50.8	0.07	127
75% siltstone + 25% tailings (<i>n</i> =3)	5.82	0.15	339	4.41	5.64	2.08	3.57	219	658	0.13	115	0.16	259
50% siltstone + 50% tailings (<i>n</i> =1)	6.19	<0.05	114	3.02	8.11	1.04	4.18	151	547	2.07	137	0.22	342
85% siltstone + 15% waste rocks (<i>n</i> =4)	5.62	<0.05	84.1	4.20	5.09	0.63	4.67	<100	401	0.15	49.2	<0.05	159
75% siltstone + 25% waste rocks (<i>n</i> =2)	6.14	<0.05	63.5	2.84	4.43	0.41	3.87	<100	338	0.78	53.7	0.05	90.3
50% siltstone + 50% waste rocks (<i>n</i> =5)	6.30	<0.05	34.1	1.03	7.41	0.17	4.99	<100	329	0.42	71.6	0.06	230
100% limestone + 5 g Trifos (<i>n</i> =4)	7.47	<0.05	1.82	<1	0.79	<0.1	2.91	<100	18.4	1.51	0.51	<0.05	13.6
85% limestone + 15% tailings + 5 g Trifos (<i>n</i> =4)	7.54	<0.05	2.49	<1	1.88	<0.1	3.32	<100	34.2	1.31	0.91	<0.05	121
75% limestone + 25% tailings + 5 g Trifos (<i>n</i> =4)	7.51	<0.05	2.14	<1	2.37	<0.1	3.28	<100	44.7	1.23	0.87	<0.05	121
50% limestone + 50% tailings + 5 g Trifos (<i>n</i> =3)	7.52	<0.05	6.84	<1	3.65	<0.1	3.35	<100	69.3	1.74	3.48	<0.05	146
25% limestone + 75% tailings + 5 g Trifos (<i>n</i> =4)	6.92	<0.05	3.21	3.27	5.87	0.68	4.28	<100	250	2.77	2.09	0.06	205
100% tailings + 5 g Trifos (<i>n</i> =1)	6.29	<0.05	9.42	2.85	7.62	2.71	3.41	<100	581	1.27	19.8	0.14	390
100% tailings + 10 g Trifos (<i>n</i> =3)	6.07	<0.05	6.60	8.15	2.47	3.01	4.19	<100	673	2.80	7.10	0.18	339
100% waste rocks + 5 g Trifos (<i>n</i> =4)	6.72	<0.05	2.70	8.64	1.68	1.31	6.36	<100	187	4.08	3.99	0.61	130
100% waste rock + 10 g Trifos (<i>n</i> =3)	6.45	<0.05	6.52	15.1	0.82	1.27	6.39	<100	248	3.68	3.22	0.17	108
100% tailings + 20 g Trifos + 20 g MKP (<i>n</i> =0): no growth	5.56												
100% waste rocks + 20 g Trifos + 20 g MKP (<i>n</i> =0): no growth	5.55												
85% limestone + 15% waste rocks + 5 g Trifos (<i>n</i> =3)	7.52	<0.05	1.66	<1	0.69	<0.1	2.83	<100	20.3	0.97	0.30	<0.05	38.4
75% limestone + 25% waste rocks + 5 g Trifos (<i>n</i> =4)	7.78	<0.05	1.51	<1	1.16	<0.1	2.85	<100	27.2	0.91	0.51	<0.05	58.1
50% limestone + 50% waste rocks + 5 g Trifos (<i>n</i> =4)	7.68	<0.05	3.11	<1	1.24	<0.1	3.42	<100	36.1	1.58	1.32	<0.05	85.5
25% limestone + 75% waste rocks + 5 g Trifos (<i>n</i> =4)	7.18	<0.05	3.78	2.58	1.82	0.22	5.40	<100	95.8	2.09	6.23	0.06	123

n number of pots with samples composited

Table 7 Trace element concentrations (mg/kg in dry matter) in shoots of Barley Mitchell grass, growing in various substrates

Substrate	pH	Ag	Al	As	Cd	Co	Cu	Fe	Mn	Ni	Pb	Sb	Zn
100% limestone (<i>n</i> =5)	7.89	<0.05	146	1.94	0.94	0.68	9.14	213	49.5	6.24	5.53	0.08	25.1
85% limestone + 15% tailings (<i>n</i> =5)	7.76	<0.05	44.8	2.01	2.46	0.13	6.35	116	42.9	2.12	6.15	0.14	254
75% limestone + 25% tailings (<i>n</i> =5)	7.74	0.08	73.6	3.37	2.92	0.67	11.8	195	80.0	5.07	17.5	0.34	376
50% limestone + 50% tailings (<i>n</i> =5)	7.75	0.08	52.9	1.82	5.86	0.48	9.20	158	159	5.50	42.5	0.42	523
85% limestone + 15% waste rocks (<i>n</i> =5)	7.93	<0.05	109	2.78	1.09	0.41	9.36	195	19.2	3.82	5.07	0.38	85.2
75% limestone + 25% waste rocks (<i>n</i> =5)	7.89	<0.05	62.6	2.61	1.21	0.31	7.67	118	16.7	2.16	5.22	0.19	100
50% limestone + 50% waste rocks (<i>n</i> =5)	7.90	0.06	74.7	1.17	1.81	0.13	6.05	138	31.2	1.22	28.2	0.26	131
100% siltstone (<i>n</i> =0): no growth	4.63												
100% siltstone + 10 g Trifos (<i>n</i> =0): no growth	4.65												
85% siltstone + 15% tailings (<i>n</i> =4)	5.60	<0.05	na	4.75	4.36	2.37	3.96	na	909	0.79	83.0	0.11	179
75% siltstone + 25% tailings (<i>n</i> =3)	5.82	<0.05	125	2.42	8.60	3.55	3.38	97.3	892	0.51	123	0.14	371
50% siltstone + 50% tailings (<i>n</i> =0) no growth	6.13												
85% siltstone + 15% waste rocks (<i>n</i> =3)	5.70	<0.05	na	3.07	4.15	0.77	4.18	122	578	0.39	47.9	0.11	78.0
75% siltstone + 25% waste rocks (<i>n</i> =3)	6.02	<0.05	94.0	3.66	5.92	0.74	5.20	97.9	747	<0.1	78.9	0.09	116
50% siltstone + 50% waste rocks (<i>n</i> =3)	6.30	<0.05	103	1.33	10.1	0.31	6.61	129	534	0.41	136	0.07	324
100% limestone + 5 g Trifos (<i>n</i> =4)	7.59	<0.05	13.2	<1	0.43	<0.1	4.80	<100	38.2	1.46	0.59	<0.05	17.7
85% limestone + 15% tailings + 5 g Trifos (<i>n</i> =4)	7.47	<0.05	10.9	<1	1.13	<0.1	4.68	<100	66.9	1.25	1.48	<0.05	88.8
75% limestone + 25% tailings + 5 g Trifos (<i>n</i> =4)	7.39	<0.05	7.06	1.18	1.91	<0.1	4.71	<100	135	1.13	1.89	<0.05	136
50% limestone + 50% tailings + 5 g Trifos (<i>n</i> =1)	7.50	<0.05	9.60	2.52	4.11	<0.1	5.65	<100	258	0.81	5.43	<0.05	192
25% limestone + 75% tailings + 5 g Trifos (<i>n</i> =1)	7.02	<0.05	7.61	4.13	8.07	0.59	5.47	<100	413	1.34	6.75	<0.05	298
100% tailings + 5 g Trifos (<i>n</i> =0) no growth	5.98												
100% tailings + 10 g Trifos (<i>n</i> =7)	6.12	<0.05	6.44	8.96	5.21	5.89	4.53	<100	1012	3.72	10.3	0.28	509
100% waste rocks + 5 g Trifos (<i>n</i> =2)	6.73	<0.05	14.9	11.0	2.15	2.28	6.08	<100	411	8.18	3.53	0.62	116
100% waste rock + 10 g Trifos (<i>n</i> =8)	6.39	<0.05	13.1	14.4	0.98	2.68	5.81	<100	471	5.72	4.74	0.26	100
100% tailings + 20 g Trifos + 20 g MKP (<i>n</i> =0): no growth	5.53												
100% waste rocks + 20 g Trifos + 20 g MKP (<i>n</i> =0): no growth	5.55												
85% limestone + 15% waste rocks + 5 g Trifos (<i>n</i> =4)	7.84	<0.05	5.45	1.17	0.74	<0.1	3.61	<100	41.1	0.73	0.51	<0.05	57.1
75% limestone + 25% waste rocks + 5 g Trifos (<i>n</i> =4)	7.76	<0.05	5.86	<1	0.58	<0.1	3.66	<100	40.2	0.82	0.63	<0.05	67.1
50% limestone + 50% waste rocks + 5 g Trifos (<i>n</i> =4)	7.45	<0.05	5.93	<1	0.92	<0.1	4.10	<100	63.1	1.29	1.80	<0.05	57.2
25% limestone + 75% waste rocks + 5 g Trifos (<i>n</i> =3)	7.14	<0.05	12.7	2.17	0.99	0.16	6.29	<100	102	2.08	4.17	<0.05	82.7

n number of pots with samples composited, *na* not analysed

a wide range of metal concentrations in the substrate. The indicators tend to translocate and accumulate metals in the above-ground plant parts. The metal concentrations in these plants reflects the metal concentration in the substrate, that is, the plant to substrate metal concentration ratio is relatively constant and there is a linear relationship between the elemental content in the plants and the concentration of the same element in the substrate (Baker 1981; Brooks 1998). Accumulators are those species that display an extreme metal uptake and translocation into the shoots (Brooks 1998).

The recognition of indicator, excluder and accumulator plants has generally relied on a comparison of the metal concentration in the plant to the total metal concentration in the substrate (e.g. Lintern et al. 1997; Nkoane et al. 2005; Yoon et al. 2006). Such calculations allow an evaluation of the translocation of metals from the substrate to the plants and the recognition of metal exclusion or accumulation behaviour. Correlation coefficients have been calculated for total metal concentrations in the substrate and the plant samples (Table 8). The data demonstrate largely insignificant correlations between these two parameters. The lack of correlation suggests that the form of the metals in the substrate has a critical influence on their phytoavailability and uptake by the plants. Hence, it may be preferable to compare the total metal content of the plant with the bio-available metal in the substrate, rather than the total metal content in the substrate. In this study, correlation coefficients between the plant chemistry and the DTPA and EDTA extracts have been calculated for all plant samples (Table 8). The calculations indicate that all plant species show moderate ($R>0.5$) to strong ($R>0.9$) positive correlation for Cd, Co, Mn, Pb and Zn (Table 8). By contrast, there are no distinct correlations for As, Cu, Ni and Sb in plant tissue and EDTA extracts for all Mitchell grasses, whilst the As content of Bull Mitchell and to a lesser degree of Barley Mitchell grass shows an improved correlation with the DTPA extract. The similar correlations coefficient values between the DTPA and EDTA extracts and the plant tissue of the Mitchell grasses indicate that the investigated plant species obtain and accumulate metals similarly. This is most likely due to similarities in plant species physiology.

The significant correlation between EDTA and DTPA extractable substrate metal and plant metal con-

Table 8 Correlation coefficients between total elements as well as EDTA and DTPA extractable elements in the substrate and their concentration in plant tissues (significance level 0.05)

Substrate	Bull Mitchell	Curley Mitchell	Barley Mitchell
Total elements			
As	0.77	ns	0.53
Cd	0.62	ns	ns
Co	ns	ns	ns
Cu	ns	ns	ns
Mn	0.71	ns	ns
Ni	ns	ns	ns
Pb	0.55	ns	ns
Sb	ns	ns	ns
Zn	0.57	0.42	0.42
EDTA extractable elements			
As	ns	ns	ns
Cd	0.98	0.75	0.62
Co	0.94	0.76	0.70
Cu	ns	0.50	0.48
Mn	0.97	0.87	0.83
Ni	ns	ns	ns
Pb	0.81	0.76	0.70
Sb	ns	ns	0.41
Zn	0.87	0.76	0.74
DTPA extractable elements			
As	0.92	0.39	0.65
Cd	0.94	0.70	0.49
Co	0.95	0.75	0.64
Cu	ns	0.50	0.47
Mn	0.97	0.85	0.82
Ni	ns	ns	ns
Pb	0.75	0.76	0.94
Sb	ns	ns	ns
Zn	0.92	0.85	0.78

ns not significant

centrations demonstrates that much of the substrate derived metals is taken up by Mitchell grasses growing in the mineralised materials. In particular, the grasses show significant and consistently high correlation coefficients for Cd, Co, Mn, Pb and Zn. Their metal concentrations linearly increase with EDTA and DTPA extractable substrate metal concentrations (Figs. 2 and 3). Hence, Mitchell grasses are indicator species for Cd, Co, Mn, Pb and Zn and seem excellent sample media for predicting Pb–Zn mineralised soils and rocks.

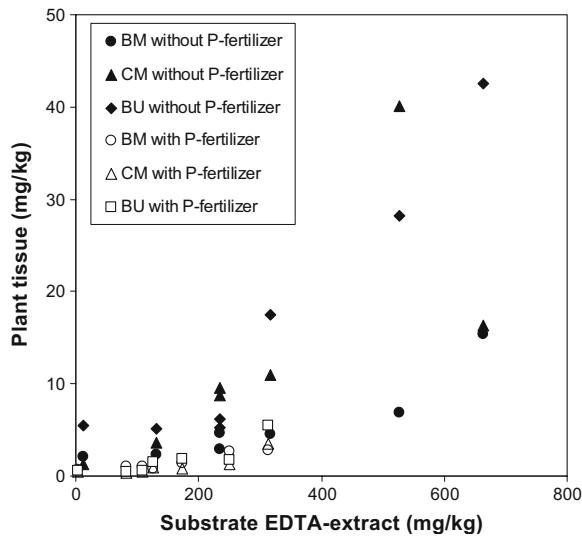


Fig. 2 Relationship between the EDTA extractable Pb concentrations in limestone-tailings and limestone-waste rock substrates (with and without phosphate fertilizer amendments) and the Pb concentrations in plant foliage (*BU* Bull Mitchell grass, *CM* Curley Mitchell grass, *BM* Barley Mitchell grass)

4.2 Zoo- and Phytotoxicity

Mitchell grasses tolerated the entire range of metal concentrations investigated, although germination did

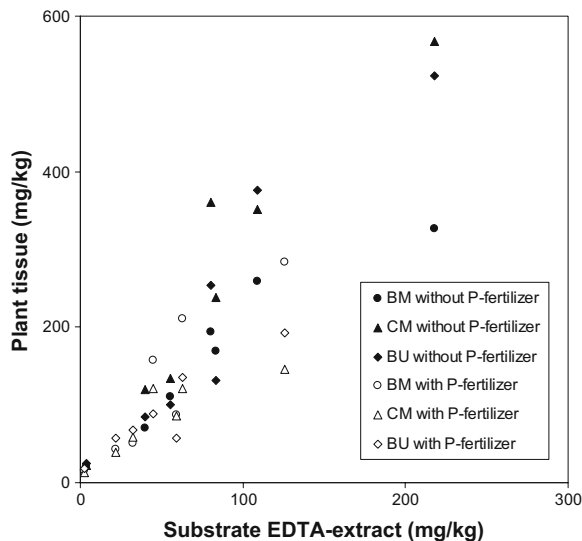


Fig. 3 Relationship between the EDTA extractable Zn concentrations in limestone-tailings and limestone-waste rock substrates (with and without phosphate fertilizer amendments) and the Zn concentrations in plant foliage (*BU* Bull Mitchell grass, *CM* Curley Mitchell grass, *BM* Barley Mitchell grass)

not occur in acidified siltstone substrates and substrates with a higher fertilization rate. The species accumulated Cd, Co, Mn, Pb and Zn with increasing bio-availability of these elements. Pronounced Pb and Zn accumulation occurred in substrates comprising tailings or siltstone-amended tailings and waste rocks as well as limestone-amended tailings (Tables 5, 6 and 7).

The regions surrounding the Cannington mine site support pastoral systems (i.e. sheep and cattle grazing), and the maintenance of biological diversity as stipulated in the environmental management plans for the Cannington mine involves the use of native flora including Mitchell grasses for revegetation. Therefore, if Mitchell grasses used for mined land reclamation at Cannington would accumulate large quantities of metals in their tissue, it may cause harmful effects on animals feeding on them (cf. Bruce et al. 2003).

Concentrations of metals in vegetation were evaluated in terms of maximum allowable dietary levels in livestock (National Research Council 2005; Table 9). The Zn concentrations in the three Mitchell grasses growing on the different substrates invariably exceed the maximum tolerable concentrations of Zn in the diet of sheep and cattle (Table 9). In particular, the Zn contents in the perennial grasses growing on tailings as well as siltstone- and limestone-tailings mixtures

Table 9 Maximum tolerable concentrations of trace elements in the diet of sheep and cattle (NRC 2005) and the approximate concentration ranges of trace elements in mature leaf tissue generalised for various species (Kabata-Pendias and Pendias 2001)

Trace element	Maximum tolerable levels		Excessive or toxic concentrations of trace elements in mature leaf tissue
	Sheep	Cattle	
Al	1,000	1,000	–
As	30	30	5–20
Cd	10	10	3–30
Co	25	25	15–50
Cu	15	40	20–100
Mn	2,000	2,000	400–1,000
Ni	100	100	10–100
Pb	100	100	30–300
Zn	300	500	100–400

All values in mg/kg in dry matter

are in excess of the maximum tolerable Zn concentrations in the fodder for sheep suggested by the National Research Council (2005). Also, the Pb levels in Curley Mitchell grasses growing on siltstone-amended tailings and waste rocks exceed the tolerable Pb concentrations in the diet of sheep and cattle (Table 9).

Concentrations of metals in the Mitchell grasses were also evaluated in terms of plant sufficiency and excess (Table 9). Potentially phytotoxic Zn levels (i.e. 100 to 400 mg/kg) were reached in Mitchell grasses growing on various substrates, whilst the concentrations of Al, As, Cd, Co, Cu, Ni, Pb and Sb were not excessive.

4.3 Implications for Capping Strategies of Mine Wastes

The results obtained in this study imply that direct seeding and propagation of Mitchell grasses in pure tailings as well as siltstone- and limestone-amended tailings may be unsustainable. Mitchell grasses are not suitable for the revegetation of pure or amended tailings as these metal-tolerant indicator plants could transfer metals into grazing animals.

Also, the revegetation of capped tailings with Mitchell grasses, where no unmineralised capillary break exists between the waste and the cover material, may not be sustainable in the long term. Mitchell grasses have a significant root penetration depth and a tendency to concentrate bio-available metals into roots and then to translocate these into the above-ground biomass (Gilfedder and Lottermoser 2008). In particular, Curley and Bull Mitchell grass have very high Pb translocation factors (metal concentration ratio of plant foliage to roots) of 7.5 and 8.1, respectively (Gilfedder and Lottermoser 2008). This distinct bio-concentration and translocation of metals coupled with the significant root penetration depth could result in phyto- and zootoxic metal levels in the above-ground biomass of Mitchell grasses, even if the metal-rich waste would be physically isolated at depth. Therefore, the design of the capping sequence for a tailings storage facility has to consider the metal uptake and root penetration depth of Mitchell grasses. For example, the use of a capping sequence incorporating a coarse-grained unmineralised hydraulic barrier and an underlying fine-grained unmineralised clay horizon would provide a more robust capping

system. These layers would limit the interaction of metal-rich solutions with plant roots and restrict the root penetration depth to unmineralised materials, reducing metal uptake of the Mitchell grasses.

An alternative to the installation of such unmineralised capping materials may be the addition of phosphate amendments to the upper tailings piles. Previous research has already documented that in situ stabilisation of Pb-contaminated soils can be accomplished by adding phosphate compounds which in turn reduced the bio-availability of Pb to plants (cf. Laperche et al. 1997; Hettiarachchi and Pierzynski 2002). Similarly, this study has demonstrated that phosphate additions to substrates reduced the bio-availability of Pb and Zn in tailings and waste rocks. Hence, Mitchell grasses growing on such phosphate-amended substrates acquired much lower metal concentrations (Tables 5, 6 and 7). The Pb concentrations of such Mitchell grasses did not exceed the recommended levels for livestock and did not reach phytotoxic concentrations (Table 9). Hence, phosphate amendments to mine wastes may represent an alternative remediation strategy to reduce the transfer of metals into the above-ground biomass of Mitchell grass species. Such an alternative capping strategy may achieve the biological isolation of the waste. Yet, further research and field trials need to establish whether phosphate amendments achieve a reduction in bio-availability and uptake of metals by plants in the long term and how phosphate-amended wastes weather under changing climatic, physical and chemical conditions.

5 Conclusions

This study was conducted to explore the use of Mitchell grasses for mined land rehabilitation at the Cannington Ag–Pb–Zn mine. Most importantly, the study sought to determine the metal tolerance and uptake of Mitchell grasses when grown through greenhouse pot trials on Cannington tailings and waste rocks containing variable amounts of phosphate fertilizer and locally available siltstone and limestone amendments. The objective of conducting such phytoremediation studies was to generate data relating to the implementation and effectiveness of capping and revegetation strategies for mine waste repositories.

This project yielded a number of important facts and implications for mined land reclamation activities

at Cannington as well as metalliferous mine sites located in regions of native grasslands, including:

1. Mitchell grasses are metal-tolerant indicator plant species with a significant root penetration depth and high translocation and bio-concentration factors. Hence, Mitchell grasses have the ability to accumulate significant concentrations of metals into their above-ground biomass.
2. Concentrations of metals in Mitchell grasses were evaluated in terms of maximum allowable dietary levels in livestock (National Research Council 2005). The pot trials revealed that if Mitchell grasses were to be used for mined land reclamation and were grown on metalliferous substrates, the grasses could potentially accumulate large quantities of Zn in their tissue, potentially causing harmful effects on animals feeding on them. Hence, it is undesirable that Mitchell grasses are grown on and their root system come in contact with tailings containing elevated levels of Zn. Otherwise, the species may accumulate phyto- and zootoxic concentrations of Zn.
3. The metal tolerance, the tendency to accumulate metals in the above-ground biomass and the significant root penetration depth of Mitchell grasses have implications for the design of waste repository covers. For example, if the covers of waste repositories were constructed without capillary breaks or clay layers, then there is the potential for deep-rooted Mitchell grasses to puncture the capping and to transfer bio-available metals from the tailings or mineralised waste rocks into their above-ground biomass. Hence, capping of waste repositories using a cover system without capillary breaks, clay layers or alternative strategies may not be sustainable in the long term.
4. The application of phosphate amendments to tailings and waste rocks may represent an alternative strategy to limit the uptake of metals by Mitchell grasses. The pot trials demonstrate that the addition of phosphate to Cannington mine wastes decreases the bio-availability of metals in these materials and reduces the Pb and Zn concentration in Mitchell grasses growing on them. Thus, the addition of phosphate amendments to the top layers of tailings may represent an alternative waste management strategy.

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References

- Baker, A. J. M. (1981). Accumulators and excluders—strategies in the response of plants to heavy metals. *Journal of Plant Nutrition*, 3, 643–654. doi:10.1080/01904168109362867.
- Berkman, D. A. (2001). *Field geologists' manual*. Melbourne: Australasian Institute of Mining and Metallurgy.
- Bodon, S. B. (1998). Paragenetic relationships and their implications for ore genesis at the Cannington Ag–Pb–Zn deposit, Mount Isa Inlier, Queensland, Australia. *Economic Geology and the Bulletin of the Society of Economic Geologists*, 93, 1463–1488.
- Brooks, R. R. (1998). Biogeochemistry and hyperaccumulators. In R. R. Brooks (Ed.), *Plants that hyperaccumulate heavy metals* (pp. 95–118). CAB International: Oxford.
- Bruce, S. L., Noller, B. N., Grigg, A. H., Mullen, B. F., Mulligan, D. R., Ritchie, P. J., et al. (2003). A field study conducted at Kidston Gold Mine, to evaluate the impact of arsenic and zinc from mine tailing to grazing cattle. *Toxicology Letters*, 137, 23–34. doi:10.1016/S0378-4274(02)00378-8.
- Burgos, P., Perez-de-Mora, A., Madejon, P., Cabrera, F., & Madejon, E. (2008). Trace elements in wild grasses: a phytoavailability study on a remediated field. *Environmental Geochemistry and Health*, 30, 109–114. doi:10.1007/s10653-008-9135-3.
- Carroll, C., Merton, L., & Buger, P. (2000). Impact of vegetative cover and slope on runoff, erosion, and water quality for field plots on a range of soil and spoil materials on central Queensland coal mines. *Australian Journal of Soil Research*, 38, 313–327. doi:10.1071/SR99052.
- Gilfedder, B. S., & Lottermoser, B. G. (2008). Biogeochemical evaluation of soil covers for base metal tailings, Ag–Pb–Zn Cannington mine, Australia. In O. Stefansson (Ed.), *Geochemistry research advances* (pp. 181–190). New York: Nova Science.
- Grant, C. D., Campbell, C. J., & Charnock, N. R. (2002). Selection of species suitable for derelict mine site rehabilitation in New South Wales, Australia. *Water, Air, and Soil Pollution*, 139, 215–235. doi:10.1023/A:1015860025136.
- Harris, D. L., & Lottermoser, B. G. (2006a). Evaluation of phosphate fertilizers for ameliorating acid mine waste. *Applied Geochemistry*, 21, 1216–1225. doi:10.1016/j.apgeochem.2006.03.009.
- Harris, D. L., & Lottermoser, B. G. (2006b). Phosphate stabilization of polymineralic mine wastes. *Mineralogical Magazine*, 70, 1–13. doi:10.1180/0026461067010309.
- Harwood, M. R., Hacker, J. B., & Mon, J. J. (1999). Field evaluation of seven grasses for use in the revegetation of lands disturbed by coal mining in central Queensland. *Australian Journal of Experimental Agriculture*, 39, 307–316. doi:10.1071/EA98119.
- Hettiarachchi, G. M., & Pierzynski, G. M. (2002). In situ stabilization of soil lead using phosphorus and manganese

- oxide: influence of plant growth. *Journal of Environmental Quality*, 31, 564–572.
- Kabata-Pendias, A., & Pendias, H. (2001). *Trace elements in soils and plants* (3rd ed.). Boca Raton: CRC.
- Keeling, S. M., & Werren, G. (2005). Phytoremediation: the uptake of metals and metalloids by Rhodes grass grown on metal-contaminated soil. *Remediation*, 15, 53–61. doi:10.1002/rem.20042.
- Laperche, V., Logan, T. J., Gaddam, P., & Traina, S. J. (1997). Effect of apatite amendments on plant uptake of lead from contaminated soil. *Environmental Science & Technology*, 31, 2745–2753. doi:10.1021/es961011o.
- Lintern, M. J., Butt, C. R. M., & Scott, K. M. (1997). Gold in vegetation and soil—three case studies from the goldfields of southern Western Australia. *Journal of Geochemical Exploration*, 58, 1–14. doi:10.1016/S0375-6742(96)00034-9.
- Mains, D., Craw, D., Rufaut, C. G., & Smith, C. M. S. (2006). Phytostabilization of gold mine tailings from New Zealand. Part 2: Experimental evaluation of arsenic mobilization during revegetation. *International Journal of Phytoremediation*, 8, 163–183. doi:10.1080/15226510600742559.
- Mallet, K., & Orchard, A. E. (2002). *Flora of Australia, volume 43, Poaceae 1: Introduction and atlas*. Melbourne: ABRS.
- Morin, K. A., & Hutt, N. M. (1997). *Environmental geochemistry of minesite drainage*. Vancouver: MDAG.
- Mulligan, D. (1998). Industry practice and research for establishment and growth of vegetation on tailings in Queensland and the Northern Territory. In C. J. Asher, & L. C. Bell (Eds.), *Proceedings of workshop on future directions in tailings environmental management* (pp. 159–166). ACMER: Brisbane.
- National Research Council (NRC) (2005). *Mineral tolerance of animals* (2nd ed.). Washington: National Academy of Sciences.
- Nkoane, B. B. M., Sawula, G. M., Wibetoe, G., & Lund, W. (2005). Identification of Cu and Ni indicator plants from mineralized locations in Botswana. *Journal of Geochemical Exploration*, 86, 130–142. doi:10.1016/j.gexplo.2005.03.003.
- Prasad, M. N. V. (2006). Stabilization, remediation, and integrated management of metal-contaminated ecosystems by grasses (Poaceae). In M. N. V. Prasad, R. Naidu, & K. S. Sajwan (Eds.), *Trace elements in the environment: biogeochemistry, biotechnology, and bioremediation* (pp. 405–424). Boca Raton: CRC.
- Rayment, G. E., & Higginson, F. R. (1992). *Australian laboratory handbook of soil and water chemical methods*. Port Melbourne: Inkata.
- Schroeder, K., Rufaut, C. G., Smith, C., Mains, D., & Craw, D. (2005). Rapid plant-cover establishment on gold mine tailings in southern New Zealand: Glasshouse screening trials. *International Journal of Phytoremediation*, 7, 307–322. doi:10.1080/16226510500327178.
- Walters, S., & Bailey, A. (1998). Geology and mineralization of the Cannington Ag–Pb–Zn deposit: an example of Broken Hill-type mineralization in the Eastern succession, Mount Isa Inlier, Australia. *Economic Geology and the Bulletin of the Society of Economic Geologists*, 93, 1307–1329.
- Yoon, J., Cao, X., Zhou, Q., & Ma, L. Q. (2006). Accumulation of Pb, Cu, and Zn in native plants growing on a contaminated Florida site. *The Science of the Total Environment*, 368, 456–464. doi:10.1016/j.scitotenv.2006.01.016.