UPTAKE OF ARSENIC BY NATIVE PLANTS GROWING ON GOLD TAILINGS IN WESTERN AUSTRALIAN RANGELANDS¹

J. Costello, H. Lacy, Z. Rengel, D. Jasper, and M. Quaghebeur²

Abstract. The natural concentration of arsenic in soils may range from 1-40 mg/kg, whereas soils overlying sulphide ore deposits in Western Australia may contain several hundred mg arsenic per kg. The greater concentration of arsenic exists within the orebodies and their immediate surrounds, and values in the thousands of mg/kg are often recorded. As a result, high arsenic levels are often found in gold tailings milled from these orebodies. Environmental considerations require that local native species are established on tailings storage facilities (TSF). Uptake of arsenic by these plants is a concern, but there is little information available to allow the potential risks to be assessed in an Australian context.

A glasshouse experiment was conducted using arsenic–rich gold tailings as the growth medium. The aim was to determine if native plants accumulate arsenic, and their growth response in the tailings. A complementary field survey assessed accumulation of metals in native plant species growing on historic and more recent TSF's in the Western Australian rangelands. In the glasshouse experiment, survival and growth of native species was far greater on low-arsenic material than on the arsenic-rich tailings. All the plants that survived in the tailings took up arsenic with concentrations ranging from 6 to 66 mg/kg, depending on plant species and the level of phosphorus application.

In the field, there were substantial interspecific differences in the concentration of arsenic in leaf material, for plants growing in arsenic-rich materials. For example, *Atriplex* species accumulated relatively little arsenic, even at high soil concentrations. By contrast, another chenopod, *Maireana pyramidata*, appeared to consistently take up larger quantities. Species of other genera appeared to fall in a range between these two. In preliminary comparisons of washed and unwashed *Atriplex* plants, it appeared that considerable quantities of arsenic may

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be also found on leaf surfaces. If confirmed, then arsenic that wildlife may ingest by eating leaves and shoots may be 50% greater than measured in this survey.

In 2 out of 14 species grown in the glasshouse experiment in these arsenic-rich gold tailings, arsenic concentrations exceeded the ANZECC maximum tolerable dietary intake level for livestock (50 mg inorganic arsenic per kg of diet). In the field study, arsenic in leaf material of *Maireana pyramidata* also exceeded the toxicity limit. Eight out of 14 species grown in the glasshouse experiment, and plants from two genera sampled in the field, contained in excess of 20 mg/kg of arsenic.

Additional Key Words: mining, revegetation.

Introduction

Arsenic is a naturally occurring, potentially toxic element in sediments and waters of the earths crust (O'Neill, 1995). Arsenic speciation in the environment is of critical importance for its toxicity. Inorganic arsenic compounds are more toxic than organic arsenic compounds to mammals. The reduced species of inorganic arsenic, As(III), is reported to be 25 to 60 times more toxic than the oxidized species, As(V). Furthermore, As(III) is intrinsically more mobile in the soil environment (Smith et al., 1998). The toxicity of arsenic to plants is a function of the species of arsenic present and the amount of water soluble arsenic that is available for plant uptake. The availability of arsenic for plant uptake is affected by soil parameters such as pH, redox status, organic matter content, clay content, the occurrence of iron and aluminium, and the phosphorus content of soils (De Koe, 1991; Parametrix, 1995; Smith et al., 1998).

Wastes generated by the mining of gold and other base metals often contain elevated concentrations of arsenic (Bech et al., 1997; Bruce et al., 2001; De Koe, 1991; Smith et al, 1998). In Western Australia, high arsenic values are often found in the tailings-solids derived from gold deposits. The arsenic is usually derived from arsenopyrite (FeAsS) in the ore (O'Neill, 1995). Environmental considerations and regulatory commitments require that local native species are established on tailings storage facilities (TSF). Uptake of arsenic by these plants is a concern, but there is little information available to allow the potential risks to be assessed in an Australian context.

A considerable variation in plant response to arsenic has been demonstrated between species of crop plants, especially in capacity for arsenic uptake and tolerance of arsenic in plant tissue (Fergusson, 1990; Peterson et al., 1981). Plants that can survive in arsenic rich soil/tailings, and especially if they accumulate arsenic in leaves and shoots, have the potential to impact on grazing animals.

The phytotoxic effects of arsenic may result in a sudden decrease in water mobility, as suggested by root plasmolysis and discolouration (yellow-browning) followed by necrosis of leaf tips and margins (Fergusson, 1990). Symptoms can also include growth reduction, violet coloration (increased anthocyanin accumulation) and leaf wilting (Kabata-Pendias & Pendias, 1984). Seed germination can also be arrested (Fergusson, 1990). The movement of arsenic within plants is restricted, and the relative order of arsenic concentrations is usually roots>vegetative tissue>seeds and fruit, with old leaves likely to contain more arsenic than the young ones (Fergusson, 1990; Smith et al., 1998).

Although there are suggested differences in tolerance to arsenic among species, the maximum tolerable dietary intake of arsenic for livestock is 50 mg of inorganic forms per kg of diet or 100 mg of organic forms, per kg of diet (ANZECC & ARMCANZ, 2000). North American literature refers to a suggested limit of 20 mg arsenic per kg of plant-containing feedstuff for domestic livestock, and reports adverse effects in mammals at levels of 50 mg of inorganic arsenic forms per kg of feed (Koch et al., 2000). Therefore, for plants containing arsenic greater than 20 mg/kg dry weight of leaves and stems, possible effects on wildlife cannot be excluded.

In this study, a glasshouse experiment was conducted using arsenic-rich tailings as the primary growth medium. The aim was to ascertain the tolerance of native plants to arsenic contained in tailings, and to determine if plants accumulate arsenic when grown on the mine residue. In addition, a field survey was carried out to gain an understanding of the issue of bioaccumulation of arsenic by arid land native plant species growing on historic and more recent tailings storage facilities in the Western Australian rangelands.

Methods

Glasshouse experiment

In this experiment, we examined the effect of increasing additions of phosphorus on plant growth and arsenic uptake, with 14 native species growing on arsenic-rich tailings material (Table 1). The tailings material had been collected from 12 areas across a gold mine tailings facility near Leinster, Western Australia, and spread evenly into eight 50 kg containers. Plant growth in the tailings was compared to that in low-arsenic lateritic waste material, which was collected from one area on the mine.

Three samples of the tailings and one sample of the laterite waste material were analyzed for plant available nutrients using standard techniques (Page et al., 1995) (Table 2). The tailings and laterite were also analysed for total arsenic using an Inductively Coupled Plasma – Mass Spectrometer (ICP-MS) (Quaghebeur et al., 2003).

 Table 1. Species selected for planting in laterite and arsenic-rich tailings in a glasshouse experiment.

FAMILY	SPECIES	COMMON NAME
AMARANTHACEAE	Ptilotus obovatus	Cotton Bush
CHENOPODIACEAE	Atriplex nummularia	Old Man Saltbush
	Atriplex vesicaria	Bladder Saltbush
	Atriplex semilunaris	Annual Saltbush
	Maireana brevifolia	Small Leafed Bluebush
	Maireana georgei	George's Bluebush
	Maireana tomentosa	Felty Bluebush
	Maireana villosa	
MIMOSACEAE	Acacia acuminata	Fine Leaf Jam
	Acacia ligulata	Umbrella Wattle
SAPINDACEAE	Dodonea viscosa	Sticky Hopbush
	Dodonea lobulata	Bead Hopbush
PITTOSPORACEAE	Pittosporum phylliraeoides	Native Willow
CAESALPINIACEAE	Senna planitiicola	Arsenic Bush

For the pot experiment, tailings were placed into a cement mixer and mixed for 10 minutes to create a homogeneous sample. The laterite waste was passed through a 2 mm sieve to remove rocks and gravel. Pots were lined with plastic bags and each pot was filled with 1.6 kg of material. The pots were 25 cm deep, with a surface area of 49 cm². Eighty-four pots were filled with tailings and 14 were filled with laterite waste.

Table 2. Analyses on laterite and tailings material used in the glasshouse experiment (mean \pm SE, n=3).

Analysis	Tailings	Laterite*
Total Arsenic (mg/kg)	2980 ± 80	11 ±1
Nitrate Nitrogen (mg/kg)	45 ±1	26
Ammonium Nitrogen (mg/kg)	1.3 ± 0.3	1
Extractable Phosphorus (mg/kg) ¹	14 ± 1	3
Extractable Potassium $(mg/kg)^1$	1000 ± 10	173
Extractable Sulphur $(mg/kg)^2$	527 ±2	5,200
Organic Carbon (g/kg)	2.3 ± 0.005	2.5
Conductivity $(1:5 H_2O) (dS/m)$	1.09 ± 0.08	3.58
pH (1:5 CaCl ₂)	8.1 ± 0.1	7.6
pH (1:5 H ₂ O)	8.5 ± 0.06	7.8
Exch. Calcium (cmol(+)/kg)	2.37 ± 0.2	12.6
Exch. Magnesium (cmol(+)/kg)	0.30 ± 0.03	4.99
Exch. Sodium (cmol(+)/kg)	2.81 ± 0.1	5.18
Exch. Potassium $(cmol(+)/kg)$	0.28 ± 0.02	0.36
Texture ³	Light Clay	Medium Clay
		with gravels
	1 1	1 1

*For all analyses except Total Arsenic, only 1 rep was analyzed.

¹Colwell (1963), ²Anderson et al. (1992), ³McDonald et al. (1998).

Fertilizer treatments were applied to the pots prior to planting (Table 3). The g/kg of fertilizer for the glasshouse situation was converted from kg/ha in the field situation using a general conversion factor of 2 million kg of soil per hectare. A higher rate of Agrich® was applied to the laterite than to the tailings, because the laterite contained lower levels of nitrate than the tailings (Table 3). The Agrich® and Double Phosphate fertilizers were dissolved separately in water and added. For the tailings, each species was grown in two replicate pots at each phosphorus level.

Table 3. Fertilizer treatments applied to tailings and laterite in the glasshouse experiment (kg/ha).

Fertilizer		Tailings		Laterite waste
	\mathbf{P}_1	P_2	P ₃	
Agrich® (11.5%N, 11.4%P)	50	50	50	100
Double Phos (18%P)	0	50	100	50

Before planting, pots containing laterite and tailings were brought to field capacity, and were maintained at these water contents throughout growth. The field capacities of the tailings and laterite waste material were determined by subjecting saturated soil samples to 10 kPa suction for 5 days (Page et al., 1995).

To ensure adequate plant numbers, seed was pre-germinated and planted into the pots when the radicle was 2 mm in length. The pots were then sealed to prevent moisture loss and maintain a high level of humidity for early growth. The pots were arranged in the glasshouse in a randomized block design. Once the seedlings had fully emerged, the bags were opened and a layer of plastic beads (1 cm deep) was placed on the soil surface to reduce evaporation and the generation of dust.

Plant deaths and discoloration in plant leaves was recorded at 3, 5, 7, and 9 weeks of growth. After 5 days, all seedlings of *Maireana brevifolia* had died in pots containing tailings, and this species was replanted. Plants were harvested 9 weeks after planting. Fresh and dry weights of shoots were recorded. The shoots were digested in concentrated nitric acid and analyzed for total arsenic using the hydride generation method on ICP-MS (Quaghebeur et al., 2003). The tailings material was also analysed for arsenic speciation using ICP-MS.

Field study

<u>Sampling.</u> Plants and soils were sampled at 18 sites in early March 2002. Sampling sites included tailings storage facilities (TSF) and unconfined tailings on active mine sites, as well as at old abandoned mines. Both capped and uncapped tailings materials were sampled. Capping is achieved by spreading local soils or mine wastes over the tailings. The sampling route through the Western Australian goldfields was via Cue, Meekatharra, Wiluna, Leonora, Kalgoorlie, and Southern Cross.

At each sampling site, two plots (2 replications) with good plant growth were chosen, and up to four species were sampled in each plot. The plots were chosen by selecting areas where groups of the same species of plants were growing in a localized area. Each plot was approximately 25 to 50 m in diameter and plots were separated by 50 m or more. The number of species sampled depended upon the number of species common to both plots. Within each plot, soils were sampled at two depths (10 cm and 50 cm) at two separate positions. Soil samples from each depth were bulked giving 2 soil samples per plot, and four soil samples per sampling site. At some sites a capping layer over the tailings material extended to a depth greater than 50 cm. In such instances, soil samples were taken at depths of 10 cm, 35 cm, and 70 cm (tailings), which resulted in 6 soil samples for those sampling sites. Soil samples were collected with a hand auger and spade and placed in plastic snap-lock bags. Approximately 300-500 g was taken for each soil sample. Soils were air dried at 40°C prior to analysis.

Plant species were identified and then sampled separately. Leaf samples were taken from plants of similar size, from the largest plants present at the site. The oldest green leaves were sampled and placed in plastic snap-lock bags. Approximately 100 g were taken for each leaf sample. At the end of each day, the plant material was washed 5 times in tap water and once in deionized water to minimize contamination of the samples by soil particles. The samples were then placed in paper bags for transportation to the laboratory. Plants were dried in a drying oven at 65°C prior to analysis.

<u>Soil and plant analysis.</u> Preliminary measurements of arsenic concentrations in soil were carried out in the field using a specially-adapted kit. This field kit provided immediate estimates of arsenic concentration, and allowed the choice of sampling sites with relatively high arsenic concentrations. The kit was adapted by Mieke Quaghebeur (PhD student – The University of Western Australia) from an arsenic kit that was designed to determine arsenic concentrations in water. This kit is still under development.

Soils from the 18 field sites were sieved to 2 mm and digested in nitric acid. Total concentrations of arsenic were then measured using ICP-MS (Quaghebeur et al., 2003). In addition, 'plant-available' arsenic was extracted from soil using the $NH_4HCO_3 - DTPA$ method (Amacher, 1996) and measured using ICP-MS (Quaghebeur et al., 2003). Measurements of pH and EC were carried out on the tailings and capping layers from the field sites using a 1:5 soil:distilled water suspension. Samples of leaf material collected at the field sites were ground to create an homogeneous sample. The sample was then digested in nitric acid and analyzed for total arsenic using ICP-MS (Quaghebeur et al., 2003).

Results and Discussion

Glasshouse Experiment

The tailings contained a high concentration of total arsenic, while the concentration in the laterite waste was low (Table 2). Plant growth and survival on the laterite material was far better than on the tailings material (Table 4). All 14 species survived on the laterite, while even at the highest rate of phosphorus, only 10 species survived in the tailings material (Table 4). These values emphasize the highly deleterious effects of these metal-rich tailings on plant growth.

Adding phosphorus to the tailings increased average plant growth and survival however, there were no clear relationships for each species between plant biomass and the rate of phosphorus applications to the tailings. The range of dry shoot weights for various plant species on the laterite was 13 to 2311 mg/plant, compared to a range of 0 to 54 mg for the tailings material, depending on phosphorus application rate.

All the plants that survived in the tailings took up arsenic, whereas plants growing in laterite material contained little or no arsenic. The concentration of arsenic in plant tops ranged from 6 to 66 mg/kg dry weight, depending on the plant species and the level of phosphorus application (Table 4). However, there was no consistent relationship between average arsenic concentration in shoots and phosphorus application to the tailings for this diverse selection of native plant species. For example, *Atriplex vesicaria* and *Maireana georgei* appeared to have reduced arsenic uptake when phosphorus application was increased (Table 4). By contrast, arsenic concentration in *Senna planiticola* increased from 6 to 36 mg/kg d.w. when the equivalent of 100 kg/ha phosphorus was added to the tailings (Table 4). The dry weight of *Senna planiticola* also decreased with increasing phosphorus application to the tailings, possibly due to arsenic toxicity. Further work is required to characterise the overall effect of phosphate application on native plant uptake of arsenic.

The interaction of arsenic and phosphorus in soil and in plant uptake is complex. In soil, similarly-charged arsenic and phosphorus species compete for sorption sites on the soil components (Peterson et al., 1981). The smaller size of the phosphate ions, compared to the

Species	Soil	Double Phos added (18% P)	Shoot dry wt j	per plant (mg)	Shoot As (mg/kg d.w.)		
•	to tailings (kg/ha)		mean	SE	mean SE		
Aca. acuminata	tailings	0	19	5	21	6	
	tailings	50	22	3	33	17	
	tailings	100	16	3	36	1	
	laterite	-	95	-	0	-	
Aca. ligulata	tailings	0	6	-	66	-	
	tailings	50	17	4	16	1	
	tailings	100	7	0	37	9	
	laterite	-	68	-	0	-	
Atr. nummularia	tailings	0	0*	-	-	-	
	tailings	50	5	0	17	1	
	tailings	100	6	-	13	-	
	laterite	-	898	-	0	-	
Atr. semilunaris	tailings	0	0*	-	-	-	
in . seminaris	tailings	50	0*	-	_	_	
	tailings	100	0*	_	_	_	
	laterite	-	1314	-	0	_	
Atr. vesicaria	tailings	0	11	5	42	6	
2111. VESICUI IU	tailings	50	14	5	42 31	3	
	tailings	50 100	14 54	5 54		3 8	
	laterite	-	54 1147	54	8 0	8 -	
Ded Jehulata							
Dod. lobulata	tailings	0	0*	-	-	-	
	tailings	50	0*	-	-	-	
	tailings	100	0*	-	-	-	
	laterite	-	65	-	1	-	
Dod. viscosa	tailings	0	0*	-	-	-	
	tailings	50	0*	-	-	-	
	tailings	100	0*	-	-	-	
	laterite	-	13	-	1	-	
Mai. brevifolia	tailings	0	0*	-	-	-	
	tailings	50	0*	-	-	-	
	tailings	100	0*	-	-	-	
	laterite	-	1011	-	0	-	
Mai. georgei	tailings	0	22	0	31	4	
	tailings	50	19	-	20	-	
	tailings	100	42	22	20	5	
	laterite	-	995	-	0	-	
Mai. tomentosa	tailings	0	8	2	35	7	
	tailings	50	16	-	43	-	
	tailings	100	11	4	26	5	
	laterite	-	667	-	0	-	
Mai. villosa	tailings	0	0*	-	-	-	
	tailings	50	16	16	8	8	
	tailings	100	6	6	15	15	
	laterite	-	2311	-	0	-	
Pit. phylliraeoides	tailings	0	9	0	28	1	
	tailings	50	10	4	36	18	
	tailings	100	15	1	33	19	
	laterite	-	56	-	1	-	
Pti. obovatus	tailings	0	0*		-	-	
1 11. 000vuills	tailings	50	2	2	32	32	
		50 100	6	$\frac{2}{0}$	52 62	32 34	
	tailings						
C 1 : 4 : 1	laterite	-	876	-	0	-	
Sen. planitiicola	tailings	0	30	3	6	1	
	tailings	50	25	0	9	3	
	tailings	100	22	2	36	7	
	laterite	-	39	-	0	-	

Table 4. Dry weights and arsenic concentration in shoots of plants grown in a glasshouse on laterite and tailings from a gold mine in Western Australia. (mean \pm standard error (SE), n=2).

*Indicates that the species died.

corresponding arsenate ions, and considerably greater concentration of phosphorus in soil, often means that the phosphate binds in preference to arsenate or arsenite. Therefore, phosphorus application to the tailings may have displaced previously bound arsenic, causing an increase in arsenic mobility (i.e. plant availability) (Kabata-Pendias and Pendias, 1984; Smith et al., 1998).

Arsenic and phosphorus are taken up by the same transporter in the root-cell plasma membrane (Peterson et al., 1981). A small amount of phosphorus is required to stimulate the transporter, thus allowing arsenic to be taken up as well. However, if the amount of available phosphorus is large, there will be competition between phosphorus and arsenic and the result may be decreased arsenic uptake (Kabata-Pendias and Pendias, 1984; Smith et al., 1998). The outcome depends on the characteristics of each plant species, therefore, the overall effect of phosphorus application on plant uptake of arsenic is difficult to predict.

Field Study

A large range of arsenic concentrations were found in the diverse tailings sites sampled. Total arsenic concentrations in tailings ranged from 119 to 4070 mg/kg, while total arsenic in capping layers ranged from 25 to 2390 mg/kg (Table 5). There was also a large range of EC values, with native plants found growing on tailings material up to 12.5 dS/m (Table 5). The tailings were circum-neutral to strongly alkaline, with the bulk of the soils occurring in the pH range 7.5 to 9 (Table 5). There was no relationship between arsenic levels in soils and EC or pH.

In general, the level of extractable arsenic in tailings tended to be higher with high total arsenic levels, particularly at 50 cm depth (Figure 1). However, there were some very clear exceptions to this trend (Figure 1). The scattering of the data could be due to different properties of the tailings at each site, such as the levels of organic matter and phosphorus, clay content, and the occurrence of iron.

There was a large range of arsenic concentrations in plants growing at the tailings sites (Table 6). For example, *Maireana pyramidata* contained up to 71 mg/kg (Table 6; Figure 2), while others, especially *Atriplex* species had very low levels, even at high concentrations of arsenic in the soil. In particular, *Atriplex nummularia* appeared best at excluding arsenic, with arsenic concentration in the plants always below 6 mg/kg, even when the total arsenic

		<u> </u>										
Site	5	Site description	1	Sample	Ext.			l As	E		pI	Η
				depth (cm)	(mg/	/kg)	(mg	/kg)	(dS/	/m)		
	con./uncon.	cap./uncap	reveg.		mean	SE	mean	SE	mean	SE	mean	SE
1	confined	capped	seeded	10	5.3	1.7	649	153	3.1	1.1	6.1	1.4
			(~4 y.o.)	50	23	9	1400	520	1.7	0.1	6.6	0.8
2A	confined	capped	seeded	10	1.8	0.1	2390	1140	1.6	0.6	8.3	0.8
A D	<u>م</u> 1	1	(~7 y.o.)	50	10	0.7	1370	47	2.4	0.8	9.2	0.0
2 B	confined	uncapped	seeded (~7 y.o.)	10 50	20 13	0.5 0.7	1980 1080	157 9	1.6 1.1	0.4 0.0	9.7 9.3	0.3 0.1
3	confined	capped	(~7 y.0.) seeded	10	2.3	1.1	523	72	3.7	1.2	7.6	0.1
5	commed	capped	(~4 y.o.)	50	10	0.4	708	487	0.6	0.0	9.7	0.2
4	confined	capped	seeded	10	4.3	2.3	906	121	5.3	2.1	8.2	0.3
•	••••••••	uppen	Sector	50	31	8	764	147	8.0	4.8	8.4	0.1
5	unconfined	uncapped	unseeded	10	43	8	1060	60	1.0	0.5	8.6	0.3
				50	69	4	1520	331	2.2	0.7	8.3	0.0
6	unconfined	uncapped	unseeded	10	14	7	4070	1710	2.6	0.2	8.4	0.0
				50	14	6	3910	2270	1.5	0.1	8.4	0.1
7	unconfined	uncapped	unseeded	10	81	31	2110	360	6.5	6.0	8.1	0.1
	~ 1			50	26	7	1450	538	5.5	3.2	7.9	0.1
8	unconfined	uncapped	unseeded	10	83	33	3080	35	3.7	1.5	8.0	0.2
0			hoboonu	50 10	86 24	<u>6</u> 3	3450 671	<u>342</u> 32	3.4	0.1	7.9 8.4	0.1
9	unconfined	uncapped	unseeded	10 50	24 33	5 5	638	32 13	1.9 2.3	0.8	8.4 8.6	0.1
10	confined	uncapped	unknown	10	3.1	0.0	605	39	6.2	1.6	8.2	0.0
10	commed	uncapped	ulikilowii	50	3.5	0.0	944	197	4.1	0.7	8.0	0.1
11	confined	uncapped	unknown	10	11	1.7	1410	405	0.1	0.0	8.6	0.1
				50	27	17	1790	737	0.3	0.1	9.0	0.0
12	confined	uncapped	unseeded	10	22	9	1380	64	1.2	0.4	8.4	0.1
				50	26	4	1540	185	10.1	7.8	8.5	0.0
14	confined	uncapped	unseeded	10	1.0	0.0	175	34	12.8	3.7	7.8	0.4
				50	0.9	0.6	132	72	5.0	0.0	8.1	0.1
17	confined	capped	unknown	10	0.6	0.1	49	3	0.3	0.0	8.9	0.2
				35	2.7	0.5	251	100	3.6	0.0	8.3	0.0
18	unconfined	unconnod	unknown	70 10	<u>69</u> 1.2	<u>15</u> 0.5	<u>1760</u> 377	47	4.9	0.1	8.1 8.5	0.1
10	uncommed	uncapped	ulikilowii	50	1.2	0.3	409	122	1.2	0.2	8.3 8.7	0.3
19	confined	capped	seeded	10	0.1	0.1	25	8	0.2	0.1	6.3	0.2
17	commea	cupped	(~5 y.o.)	50	6.6	0.1	751	1	2.7	0.4	7.6	0.0
20	confined	capped	seeded	10	0.2	0.1	28	5	11.2	1.6	8.0	0.0
		11	(~8 y.o.)	50	0.4	0.1	119	13	4.9	0.7	8.3	0.0
conf	ined/unconfi	ned: confi	ned = built	structure (genera	lly < 2	0 years	old)				
			nfined = ope						old)			
cap./	uncap.:		d = distinct					•	/			
I			be multiple									
			oped = origi		osited	tailing	gs surfa	ce				
reve	getation:		d = seeded						tities			
	-	(````				T				

Table 5. Extractable arsenic (As), total As, EC, and pH of tailings and capping layers at sites located in the rangelands of Western Australia. (mean \pm standard error (SE), n=3).

unknown = may be seeded or naturally colonized

(y.o. = years ago)

unseeded = naturally colonized

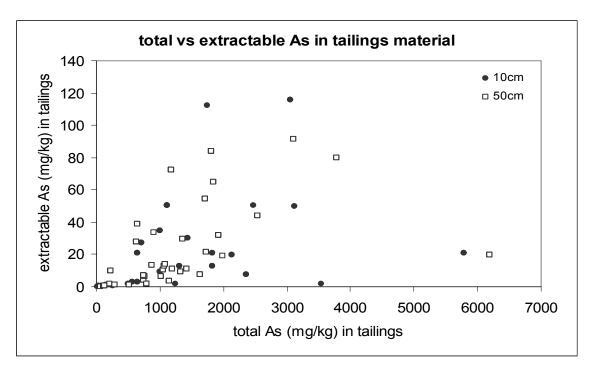


Figure 1. Total and extractable (plant available) arsenic (As) in tailings at sites located in the rangelands of Western Australia.

concentration in tailings reached 3800 mg/kg (Tables 5, 6). Arsenic concentrations in leaves of *A. vesicaria* and *A. bunburyana* did not exceed 20mg/kg (Table 6).

In contrast to the *Atriplex* species, *Maireana pyramidata* appeared to contain larger concentrations of arsenic at given low concentrations in the soil (Figure 2). There were no obvious relationships for arsenic concentration in the plants and the soil for the other species sampled. This may be due to the small number of replications available for those species.

At five of the seven capped sites (Sites 1, 3, 17, 19, and 20), the total arsenic concentration in the capping layer was lower than in the tailings below (Table 5). However, the opposite occurred at Sites 2A and 4, where the total arsenic concentrations in the top 10 cm were 2390 and 906 mg/kg respectively, with total arsenic concentrations at 50 cm depth of 1370 and 764 mg/kg respectively. This may be due to capillary rise of water bringing arsenic to the surface over time, or from contamination during or after application of the capping layer. In the case of site 2A, tailings dust was known to be deposited on the capping (H. Lacy, pers. comm., 2002).

Site	Cap./uncap.	Species	Plant As (mg/kg)		
			mean	SE	
	Capped	Atriplex bunburvana	1.8	1.1	
		Atriplex nummularia	1.6	0.8	
		Maireana pyramidata	2.0	1.0	
		Maireana triptera	2.7	2.3	
2A	Capped	Atriplex vesicaria	12	0.6	
		Maireana polypterygia	29	20	
		Maireana pyramidata	32	9	
B	Uncapped	Atriplex vesicaria	16	1	
		Maireana polypterygia	26	5	
		Maireana pyramidata	71	2	
	Capped	Atriplex nummularia	1.1	0.1	
		Atriplex vesicaria	3.5	0.3	
		Maireana pyramidata	2.5	0.3	
		Maireana triptera	1.3	0.1	
	Capped	Acacia pruinocarpa	13	8	
		Acacia victoriae	4.3	1.7	
		Atriplex nummularia	0.8	0.6	
		Maireana pyramidata	1.6	1.1	
	Uncapped	Atriplex bunburyana	8.0	0.5	
		Atriplex vesicaria	6.2	0.4	
		Halosarcia syncarpa	2.3	0.4	
		Muehlenbeckia sp.	13	1	
	Uncapped	Atriplex quinii	21	4	
	11	Halosarcia syncarpa	5.2	0.5	
		Maireana georgei	17	3	
	Uncapped	Atriplex bunburyana	4.7	0.4	
	Uncapped	Atriplex bunburyana	8.6	0.6	
	PP	Atriplex nummularia	4.5	0.9	
	Uncapped	Atriplex bunburyana	3.2	0.2	
9	Oncapped	Atriplex vesicaria	3.1	0.2	
		Halosarcia	5.0	0.2	
		Maireana pyramidata	2.8	1.0	
)	Uncapped	Atriplex bunburyana	0.9	0.1	
	Oneapped	Atriplex nummularia	0.5	0.1	
		Atriplex vesicaria	0.3 1.0	0.1	
		Eucalyptus salubris	0.7	0.2	
1	Uncapped	Alyogyne hakeifolia	13		
L	Uncapped	Atriplex stipitate	13	0.3	
			4.0	0.: 2.3	
2	Uncapped	Eucalyptus sp. Atriplex bunburyana	4.0	0.0	
2	Uncapped			0.0	
		Atriplex lentiformis	5.9 10	0.4	
4	Unconned	Atriplex stipitate	3.4	1.0	
	Uncapped	Atriplex bunburyana			
7	Capped	Atriplex bunburyana	1.2	0.2	
		Atriplex vesicaria Maincana mmamidata	1.0	0.7	
		Maireana pyramidata Maireana triptora	0.9	0.1	
)	I In a second of the	Maireana triptera	0.7	0.2	
3	Uncapped	Atriplex bunburyana	3.4	1.7	
	<u> </u>	Maireana pyramidata	42	-	
9	Capped	Acacia aneura	9.7	0.1	
		Acacia murrayana	24	0.5	
		Maireana pyramidata	7.3	1.7	
	~ .	Maireana villosa	9.0	3.1	
0	Capped	Atriplex nummularia	0.3	0.2	
		Atriplex vesicaria Maireana pyramidata	1.5	-	
			1.2	0.0	

Table 6. Arsenic (As) concentration in leaves of plants growing ontailings at sites located in the rangelands of Western Australia.

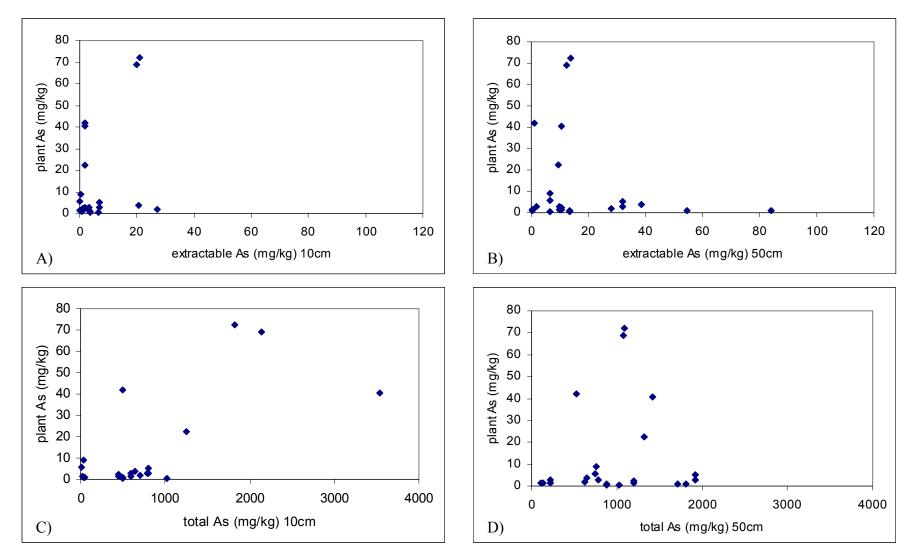


Figure 2. Arsenic (As) concentrations in leaves of *Maireana pyramidata* growing in capped or uncapped tailings, in relation to As in the soil profile. A) Extractable As at 10cm depth. B) Extractable As at 50cm depth. C) Total As at10cm depth. D) Total As at 50cm depth.

Capping layers can provide a habitat for roots of shallow-rooted species to remain in, thus minimizing penetration of roots of such species into the tailings below. This may result in lower arsenic uptake and concentrations in the foliage. As an example, arsenic concentration in leaves of *M. pyramidata* was positively related to total arsenic in the top 10 cm. Therefore, capping layers with low total arsenic appear likely to minimize arsenic uptake by this species. Arsenic concentrations in leaves of *M. pyramidata* plants growing in surface layers with up to 1,000 mg As/kg, generally remained less than 10 mg/kg. There was one exception, where 42 mg As/kg arsenic was recorded in leaves of *M. pyramidata* growing in material with total arsenic around 500 mg/kg. This site consisted of uncapped tailings of pH 8.8 and 1.36 dS/m E.C. Further work is required to ascertain factors determining arsenic uptake in the soil-plant system.

No plant species other than *M. pyramidata* showed any decrease in arsenic uptake as a result of a capping layer. For some species, this conclusion was limited by the small number of replications available. For other species, such as *Atriplex* species it may be because they only take up small amounts of arsenic, independent of the concentration in the soil.

Successful natural colonization and growth of native species on uncapped tailings material with high arsenic concentrations were observed in the field, for example Sites 5 to Sites 14 (Table 6). This was in contrast to very poor plant growth and survival in tailings with similar arsenic levels in the pot experiment. Therefore, it may be that other factors in the tailings were affecting plants in the pot experiment. Alternatively, it may be due to the adaptation of plants to arsenic in the field.

The potential for adverse health effects on biota from the arsenic in tailings needs to be further assessed. The maximum tolerable dietary intake of arsenic for livestock is 50 mg of inorganic forms per kg dry matter of 100 mg of organic forms per kg dry matter (ANZECC & ARMCANZ, 2000). Arsenic concentrations in the plant shoots grown in the glasshouse experiment in raw tailings, with no fertilizers added, ranged from 6 mg/kg dry weight in *Senna planitiicola* to 66 mg/kg dry weight in *Acacia ligulata* (Table 4). It is likely most of that arsenic was in the inorganic form (Quaghebeur et al., 2003). If this is really the case, i.e. - if all the arsenic in *A. ligulata* was in an inorganic form, it would exceed the ANZECC Guideline. In the glasshouse experiment, *Ptilotus obovatus*, with 100 kg/ha phosphorus added to the tailings, also exceeded 50 mg/kg arsenic (Table 4). Hence, out of 14 species tested, 2 exceeded the maximum tolerable concentrations of arsenic from the standpoint of dietary intake by livestock.

In the field study, *Maireana pyramidata* (71 mg/kg) (Table 6) also exceeded the 50 mg As/kg toxicity limit.

North American literature refers to a suggested limit of 20 mg/kg arsenic in fodder for domestic livestock, and reports adverse effects in mammals at feeding levels of 50 mg of inorganic arsenic forms per kg of feed (Koch et al., 2000). It is therefore suggested that a figure of 20 mg for inorganic arsenic per kg dry matter may well be a more appropriate limit for native vegetation growing on tailings. If this conservative approach was adopted, this would suggest that *Acacia acuminata*, *Aca. ligulata*, *Atriplex vesicaria*, *Maireana georgei*, *M. tomentosa*, *Pittosporum phylliraeoides*, *Ptilotus obovatus* and *Senna planitiicola* from the glasshouse experiment would contain unacceptable levels of arsenic in plant tissue (Table 4). This represents 8 out of the 10 species that survived in the Lawlers tailings. In the field study, *Maireana polypterygia*, *M. pyramidata*, and *Acacia murrayana* also exceeded the 20 mg/kg toxicity limit, which represents 2 genera at 4 of the field sites (Table 6).

In addition to the concentration of arsenic in plant material, arsenic in soil needs to be taken into account when considering potential toxicity to grazing animals. The tailings material from the glasshouse experiment contained inorganic arsenate [As(V)], which is the predominant arsenic species in well-aerated soils. As(V) is more toxic than organic arsenate (Smith et al., 1998). Since animals can directly ingest tailings material while grazing, a capping layer would prevent direct access to the tailings. In considering the effect of capping, one should keep in mind that arsenate-salts can accumulate on the surface of capping layers as a result of capillary rise, which is enhanced in arid regions such as the Western Australian goldfields, where evapotranspiration is high and exceeds rainfall.

Other factors that need to be considered when assessing the risk of contaminated tailings to biota are 1) the ingestion of tailings dust adhered to plant material, 2) the ingestion of salt on the soil surface, and 3) animals drinking from contaminated pools of water. During the field study a salt crust was observed on the soil surface at some of the sites, such as Site 1 and Site 8. Surface soil at these sites contained 649 and 3080 mg/kg total arsenic respectively (Table 5). Therefore, ingestion of both the contaminated salt and soil may be a risk for the wildlife.

Preliminary observations suggest that substantial arsenic may occur on leaf surfaces, in addition to that within the plant. At Site 1, washing of leaf material of *Atriplex* species prior to analysis removed, on average, almost 50% of total arsenic in unwashed material (data not shown). The arsenic on these leaf surfaces may be from dust adhering to the leaves, or

associated with salt exudation by these species. At this particular site, there was 649 mg total arsenic per kg in the capping layer, which may be the source of the dust on the leaves. For future research, consideration could be given to routinely analyzing unwashed plant material as this represents the total arsenic likely to be ingested during grazing.

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