PRELIMINARY INVESTIGATION OF ARSENIC AND COPPER IN PLANTS AND TAILINGS AT TELFER GOLD MINE

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EXTENDED ABSTRACT

The successful establishment of revegetation using native plants is crucial to help phytostabilization of mine tailings. To assess arsenic (As) and copper (Cu) pollution levels and the feasibility of using native plants in rehabilitation of mine areas, a preliminary investigation was conducted to measure As and Cu in mine wastes and native plants at Telfer Gold Mine. The top layer of soil/mine wastes and leaf samples of native plants (Acacia spp, Dampiera sp, Eucalyptus camaldulensis, Maireana platycarpa) were collected at the mine sites (tailings) and in the native bush outside the mine (control) and analysed for pH, total and extractable elements (including As and Cu) in soils and total concentration of elements (including As and Cu) in plants. The pH was significantly lower and the total concentrations of As and Cu greatly higher (more than 2 orders or magnitude) in tailings compared to the control soil. The extractable Cu concentrations were significantly higher in tailings than the control soil and not influenced by the type of extractant used. The extractable As concentrations were low in tailings and not detectable in the control soil. The concentrations of As and Cu in tailings exceeded the thresholds for both ecological and health investigations based on the assessment levels for soil, sediment and water for contaminated sites management (Department of Environment and Conservation, Western Australia). The concentrations of As and Cu in plant leaves were higher in mine tailings than control (the reverse was true for As in Acacia sp-1). The concentrations of As and Cu in plant leaves were very different among the plant species in the same sites. The concentrations of As and Cu in leaves of plants growing on tailings were above the normal ranges (but mostly below or within the critical phytotoxicity level) and at the maximum dietary intake levels for livestock. The relatively higher concentrations of As and Cu in un-washed leaves compared to leaves washed (1% v/v acetic acid) before analysis indicated that As and Cu could be transferred from mine site to the surrounding environments in dust. Further studies are needed to develop the science-based knowledge on how to minimise or mitigate the relevant environmental risks.

Keywords: metals, native plants, phytoremediation, rehabilitation, tailings
1. INTRODUCTION

Newcrest Mining Limited (NML) operates the Telfer Gold Mine (TGM) in Western Australia. The mine is located 485 km south east of Port Hedland on the western edge of the Great Sandy Desert. Telfer has an average annual rainfall of approximately 380 mm mostly falling between December and March. Average annual evaporation greatly exceeds rainfall at over 4,000 mm (Natural Resource Services Pty Ltd, 2005; COOE, 2008).

Geochemical characterisation of mine waste materials from TGM by Natural Resource Services Pty Ltd (2005) identified high levels of arsenic (As) and copper (Cu). The investigation by COOE (2008) has observed that the highest concentrations of As in plant leaves were in the heap leach pads and old tailings storage dams; while the highest concentrations of Cu in plants were in the heap leach pads. Arsenic and Cu have transferred from the mine sites to the surrounding areas.

Plants could mediate the transformation, mobility and bioavailability of metals, especially in the rhizosphere due to plant-soil-microbe interactions (Park et al., 2011) and root exudates. The pH is significantly lower in the rhizosphere in the bulk soil than in the rhizosphere with the metal additions (Zhang et al., 2012). The pH changes in the rhizosphere could influence As and metal speciation and bioavailability.

The plant responses to As and metals are dose-dependent (Berry and Wallace, 1981). For essential metals (i.e. Cu) these responses cover the phases from deficiency through sufficiency/tolerance to toxicity. For non-essential As and metals (i.e. Cd) only the tolerance and toxicity phases occur. The critical, or threshold, toxicity concentration in the growth substrate results in a growth decrease, and varies greatly for various metals and plant species (Reichman, 2002). In addition, the concentration at which the tolerance plateau changes to a steep decrease of the toxicity phase is also commonly used (Davies, 1993). Kopittke et al. (2010) reviewed 119 studies and reported the median toxic concentrations of As and Cu in the solution culture to be 9 and 2 µM, respectively, but toxic concentrations varied by five orders of magnitude in various studies.

The high concentrations of As and Cu in soils and plants may have hazardous consequences and pose a significant risk to humans and animals (Mendez and Maier, 2008a, b). Preliminary measurements of As and Cu in mine waste materials and native plants was started during the TGM site visit in December 2011. The objectives were to measure (i) total and extractable concentrations of As and Cu in tailings and natural topsoil; (ii) concentrations of As and Cu in leaves of different plant species; and (iii) the effect of washing leaves before analysis on concentrations of As and Cu.

2. MATERIALS AND METHODS

2.1. Sites

Three sites were selected: two tailings storage facilities (TSF) [site-1 in TSF-6 dam (Easting 51k 0416423; Northing 51k 7600217) and site-2 in the western corner of the old (>10 years) tailings storage dams] and a natural site (control) >1 km away from the mine (site-3, Easting 51k 0412347; Northing 51k 7601097). Plant species sampled at each site were listed in Table 1.

2.2. Sampling and measurement

Leaves of 6 plant species were collected together with adjacent soil/tailings (top 0-3 cm layer) on 19 December 2011. The samples were brought back to The University of Western Australia, and leaf samples were stored at 4 °C.
### Table 1. Plant species sampled at the investigation sites

<table>
<thead>
<tr>
<th>Location*</th>
<th>Botanic name</th>
<th>Common name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site-1</td>
<td>Acacia sp-1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Maireana platycarpa</td>
<td>Bluebush</td>
</tr>
<tr>
<td></td>
<td>Dampiera sp</td>
<td></td>
</tr>
<tr>
<td>Site-2</td>
<td>Eucalyptus camaldulensis ssp. refulgesis</td>
<td>River red gum</td>
</tr>
<tr>
<td>Site-3</td>
<td>Acacia sp-1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acacia sp-2</td>
<td></td>
</tr>
</tbody>
</table>

*Site-1: tailings storage facility (TSF-6); site-2: western corner of old TSF (>10 years tailings); site-3: natural area as control.

The following day leaf samples were divided into 3 subsamples, then washed prior to analysis in: (i) de-ionised (DI) water three times and Milli-Q water once (=DI water washed); (ii) DI water once, 1% (v/v) acetic acid once, DI water once and Milli-Q water once (=acetic acid washed) and (iii) not washed (=un-washed). All samples were then dried to constant weight at 60 °C for 5 days in a forced-air cabinet, and ground to pass a 0.75-mm mesh.

The concentration of elements (including As and Cu) in plant tissues was determined by ICP-OES (Optima 5300DV, PerkinElmer, Shelton, USA) after digesting plant material in a heated mixture of concentrated nitric and perchloric acids (Bassett et al., 1978).

The all soil/tailings samples were dried and sieved to pass a 2-mm sieve. The concentration of the extractable elements (including As and Cu) was measured by ICP-OES after extraction and filtration. Briefly, soil (4 g) was shaken with either DI water (20 mL) or 0.01 M CaCl₂ (20 mL) for 4 hours, or 0.05 M EDTA (pH 7.0, 20 mL) for 1 hour at 25 °C on an end-over-end shaker (McGrath, 1996). Extracts were filtered through a 0.45-μm membrane Acrodisc® syringe filter. The subsamples of soil/tailings were sent to Australian Laboratory Services (ALS) Pty Ltd, Perth, for total As and Cu analysis. The total concentrations of metals (As, Cd, Cr, Cu, Pb, Ni and Zn) were analysed by ICP-AES (Vista Pro, Varian, Melbourne, Australia) after digestion in a heated mixture of concentrated nitric (HNO₃) and hydrochloric (HCl) acids and hydrogen peroxide (H₂O₂).

## 3. Results

### 3.1. Total concentrations of As and Cu

There were higher concentrations of total As and Cu in the mine tailings compared to the control site, with extremely high Cu concentration (1,430 mg kg⁻¹) in old tailings storage facility (site-2). The total concentrations of As in the control soil (site-3) was below the detection limit (<5 mg kg⁻¹) of ICP-OES (Fig. 1).

### 3.2. The extractable As and Cu

The extractable Cu concentration was not influenced by the type of extractant used, and was extremely high at site-2. Arsenic concentrations at sites 1 and 2 decreased in the order EDTA > CaCl₂ > DI. No extractable As could be detected in the control soil (Table 2).
Fig. 1. The total concentrations of As and Cu. Site-1: tailings storage facility (TSF-6); site-2: western corner of old TSF (>10 years tailings); site-3: natural area as control (ND: not detectable, <5 mg kg⁻¹).

Table 2. The extractable As and Cu using different extractants.

<table>
<thead>
<tr>
<th>Location*</th>
<th>Method</th>
<th>Extractable As</th>
<th>Extractable Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site-1</td>
<td>DI water extractable</td>
<td>0.04</td>
<td>48.8</td>
</tr>
<tr>
<td></td>
<td>0.01 M CaCl extractable</td>
<td>0.07</td>
<td>48.7</td>
</tr>
<tr>
<td></td>
<td>0.05M EDTA extractable</td>
<td>0.23</td>
<td>46.2</td>
</tr>
<tr>
<td>Site-2</td>
<td>DI water extractable</td>
<td>ND**</td>
<td>469</td>
</tr>
<tr>
<td></td>
<td>0.01 M CaCl extractable</td>
<td>0.08</td>
<td>481</td>
</tr>
<tr>
<td></td>
<td>0.05M EDTA extractable</td>
<td>0.18</td>
<td>559</td>
</tr>
<tr>
<td>Site-3</td>
<td>DI water extractable</td>
<td>ND</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>0.01 M CaCl extractable</td>
<td>ND</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>0.05M EDTA extractable</td>
<td>ND</td>
<td>2.6</td>
</tr>
</tbody>
</table>

*Site-1: tailings storage facility (TSF-6); site-2: western corner of old TSF (>10 years tailings); site-3: natural area as control
**ND: not detectable.

3.3. The concentrations of As and Cu in leaves: the effect of washing

In most cases, the washed leaves had lower concentrations of As and Cu compared to un-washed leaves (Fig. 2). The concentration of Cu was higher in leaves after DI water than acetic acid washing, but the concentration of As varied with the washing methods (Fig. 2). Acetic acid washing decreased As concentration by more than 50% in E. camaldulensis (old tailings, site-2) and nearly 17-fold in Acacia sp-2 (control site). In contrast, the Cu concentration was less influenced by washing, with decreases of up to 9.4% with DI water and up to 18% with acetic acid washing.

3.4. The concentrations of As and Cu in leaves washed in 1% v/v acetic acid

The leaf concentrations of As and Cu were higher in plants growing in tailings than control soil (the reverse was true for As in Acacia sp-1) (Fig. 2). The concentration of Cu in plants from the tailings was 2-5 times higher than those from the control site. Compared with Cu, a wider range of As leaf concentration was observed for tailings and
the control site. The leaf concentration of Cu was highest in *M. platycarpa*, followed by *Dampiera* sp., *E. camaldulensis* and *Acacia* sp-1. The concentration of As decreased in the order *Dampiera* sp. > *M. platycarpa* > *Acacia* sp-1 > *E. camaldulensis* (Fig. 2). The concentrations of As and Cu in leaves differed among the plant species on the same site (Fig. 2). At site-1, *Dampiera* sp had higher concentration of As compared to *Acacia* sp-1 and *M. platycarpa*.

![Graph showing concentrations of As and Cu in leaves after washing](image)

**Fig. 2.** The concentrations of As (top graph) and Cu (bottom graph) in leaves after washing. Site-1: tailings storage facility (TSF-6); site-2: western corner of old TSF (>10 years tailings); site-3: natural area as control.

4. Discussion

4.1. Arsenic and Cu in tailings and soils

In the present investigation, the total As concentration was above 140 mg kg\(^{-1}\) and total Cu concentration from 180 to 1,430 mg kg\(^{-1}\) in tailings. These concentrations were within the range reported by COOR (2008), but they exceeded the thresholds for both ecological and health investigations (except Cu at site-1) (DEC, 2010, see Table 3). In particular, total As at both tailings sites was 7 times higher than the threshold for triggering the ecological intervention. The As concentration in tailings was also higher than the Spain standard threshold of 24 mg As kg\(^{-1}\) (Moreno-Jiménez et al., 2010b). Obviously, it is necessary to remediate the tailings to minimise or mitigate the environmental risks.
Table 3. Department of Environment and Conservation thresholds of As and Cu concentration for triggering soil investigation (DEC, 2010)

<table>
<thead>
<tr>
<th>Element</th>
<th>Ecological investigation level</th>
<th>Minimum health investigation level</th>
</tr>
</thead>
<tbody>
<tr>
<td>As (mg kg(^{-1}))</td>
<td>20</td>
<td>100</td>
</tr>
<tr>
<td>Cu (mg kg(^{-1}))</td>
<td>100</td>
<td>1000</td>
</tr>
</tbody>
</table>

Although total concentration of As and metals is an important criterion for the assessment and management of contaminated sites, the total element concentration is not a good indicator of As and metal mobility, availability and, therefore, risk (Moreno-Jiménez et al., 2010b). The concentrations of extracted As and metals are more suitable for evaluating their transfer from soils and tailings to surrounding ecosystems (García-Salgado et al., 2012). In the samples described here, only less than 0.03, 0.05 and 0.2% of total As could be extracted by DI water, CaCl\(_2\) and EDTA, respectively, which was in agreement with Moreno-Jiménez et al. (2010a, b) using CaCl\(_2\) or EDTA as extractants, and Costello et al. (2003) using NH\(_4\)HCO\(_3\)–DTPA method. However, more than 30% Cu was extracted by the extractants. These results indicated that As was less mobile and phytoavailable than Cu in the tailings, or that suitability of tested extractants for As is relatively poor.

There is no agreement in the literature as to which extractant most accurately estimates the phytoavailability of trace metals in soils (Menzies et al., 2007). The use of varied extractants such as neutral salt solution (i.e. CaCl\(_2\) and NH\(_4\)NO\(_3\)) and complexing agents (i.e. EDTA and DTPA) could result in extraction of different chemical fractions of metals. A study by Menzies et al. (2007) regarding the evaluation of single extractants for estimation of the phytoavailable metals in soils pointed out that neutral salt solution tended to provide the best relationship between soil extractable metals and plant tissue accumulation, whereas complexing agents or acid extractants (e.g. HCl) were generally poorly correlated to plant uptake. However, recent studies have indicated that the transformation of metals in soils is a dynamic process, meaning that metal phytoavailability changes with time (Rao et al., 2008) and is therefore difficult to measure (Moreno-Jiménez et al., 2010a).

4.2. Arsenic and Cu in plants

The concentrations of As or/and Cu in the present investigation were within the ranges reported by COOR (2008) for plants at TGM tailings, and by Costello et al. (2003) for plants in the Western Australia gold-mine tailings (e.g. 1.2–42 mg As kg\(^{-1}\) in leaves of *Maireana* spp.). Regarding plants growing on tailings at TGM, the median concentrations of As and Cu, respectively, were 2.5 and 24 mg kg\(^{-1}\) in *Acacia aneura* leaves, and 4.3 and 58 mg kg\(^{-1}\) in *Maireana platycarpa* leaves (COOR, 2008).

The concentrations of As and Cu in leaves of plants growing on tailings were above the normal ranges, but mostly below or within critical phytotoxicity thresholds, and at the maximum dietary intake levels for livestock (Chaney, 1989; see Table 4), which indicated that native plants can be used in phytostabilization of mine tailings.

Table 4. The normal concentration, phytotoxic concentrations and maximum concentration tolerated by livestock of As and Cu in plants (from Chaney, 1989)

| Element | Normal concentration (mg kg\(^{-1}\) dry foliage) | Phytotoxic concentration (mg kg\(^{-1}\) dry foliage) | Maximum concentration tolerated by livestock (mg kg\(^{-1}\) dry diet) |
|---------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------------------------
| As\(_{org.}\) | 0.01–1 | 3–10 | 50 | 50 | 50 | 50 |
| Cu | 3–20 | 25–40 | 100 | 25 | 250 | 300 |
Different plant species have variable capacity to tolerate As and metals. Hence, the critical toxicity concentration in plants varied with different plant species in literature. Nevertheless, most studies on metal toxicity have considered crop and pasture species. In contrast, Australia has many unique plant species that evolved over millions of years where increased genetic diversity, hence, adaptability, has often been advantageous (James, 1981; Coates and van Leeuwen, 1996). Unfortunately, only a few studies compared metal tolerance of Australian native species (e.g. Lamb et al., 2010a, b; Reichman et al., 2001, 2004, 2006).

4.3. Arsenic and Cu transfer via dust

The concentrations of As and Cu in leaves washed prior to analysis were relatively lower compared to those in un-washed leaves (Fig. 2), as also observed by Costello et al. (2003), whereby washing of leaves of Atriplex species prior to analysis removed, on average, almost 50% of total As as determined in un-washed leaves. Although the concentration of As in control soil was under the detection limit (<5 mg kg⁻¹), the leaves of Acacia sp-1 grown at the control site had relatively high As concentration, even higher than the species grown on tailings (site-1), indicating that As (and most probably Cu as well) could be transferred from the mine site to the surrounding environments via dust. Hence, dust control by covers such as vegetation is one of important measures to minimise As and Cu risk in mine sites as well as after mine closure (Mendez and Maier, 2008a, b).

5. CONCLUSIONS

The total concentrations of As and Cu in tailings exceeded the thresholds that would trigger both ecological and health investigations. The concentrations of As and Cu in leaves of plants growing on tailings were above the normal ranges in plants, but mostly below or within phytotoxicity levels. Arsenic and Cu could be transferred from the mine site to the surrounding areas in dust. It is important to understand the toxicity responses of Australian native species to As and metals (i.e. Cu) so that plant species and appropriate management can be identified for effective mine revegetation. Therefore, research is needed to quantify the tolerance of relevant species to a range of As and metal contamination levels.

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