Treating Fe-rich acid mine drainage with Tasmanian plants as a metal removal mechanism

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Abstract

Fe-rich legacy acid mine drainage (AMD) flowing through Tasmania's Mt Lyell copper mine, Queenstown, has low pH and high metals concentrations (550 mg/L Fe; 100 mg/L Al and Mn). Four native Tasmanian plant species (*Isolepis inundata, Juncus astreptus, Juncus pallidus, and Baloskion tetraphyllum*) were grown in two AMD solutions (AMD pre-treated with alkaline material and full-strength AMD) to test the survivability of the juvenile plants in this contaminated water. We found that metal uptake was similar for pre-treated and full-strength AMD, suggesting that pre-treating the AMD with alkaline material may not be necessary to increase metal uptake, but may increase survivability.

Keywords: Passive treatment, phytomining, phytoextraction, harvesting technique

Introduction

Fe-rich acid mine drainage (AMD) is a global threat to water quality, resulting in lifeless waterways and metal accumulation in the environment (Bell 2014; Fleming et al. 2022; Ighalo et al. 2022). Haulage Creek is the main recipient of AMD from Mt Lyell, Queenstown, Tasmania, characterised by high median Fe concentrations (≈ 550 mg/L) and low pH (3) (Nascimento et al. 2023). Traditionally, treatment would include active systems which use chemical dosing; however, the use of passive techniques, such as combining alkaline treatments and plant systems into a treatment train, could be less expensive and more appropriate for the remote mine currently in care-taker mode.

Phytoextraction is the removal of contaminants from a contaminated media using plants with the intention of remediation (Hartley 2004; Kumar and Kumar 2019; Pletsch 2003). Phytoremediation is recommended for low-to-medium contamination levels to maintain plant health (Ali et al. 2013). However, locally-adapted ecotypes of plants growing at heavily contaminated mine sites should be tested for metal uptake ability to determine their phytoextraction potential (Li et al. 2009).

Phytoextraction has been considered for both land-based (Corzo Remigio et al. 2020) and aquatic systems (Sasmaz et al. 2016), using both naturalised and invasive species (Ashraf et al. 2011; Mishra et al. 2008). However, utilising native, non-invasive species for riparian systems requires further investigation. Similarly, the harvesting strategy required for riparian systems may differ from land-based systems, especially when considering if the entire plant will be removed or only the aboveground biomass. Harvesting strategies will also affect plant survival, as removing only aboveground biomass will decrease the buffering biomass of the plant against the AMD.

Using alkaline material to pre-treat the AMD prior to contact with the plants may increase their metal uptake (Li et al. 2015). Metal uptake greatly depends on plant species, metal concentrations, and synergistic and antagonistic interactions between elements (Drzewiecka et al. 2012). This means that increasing the AMD's pH and decreasing the concentration of easily-precipitable elements, such as Fe and Al, may increase economically valuable metal uptake.

This paper investigates operational and design characteristics for a phytoextraction system for the removal of metals from Fe-rich AMD, specifically looking into: (1) the effect of inflow metal concentrations on plant metal uptake (i.e., through the presence of alkaline pre-treatments); (2) where the plants store metals (i.e. in the roots or shoots); (3) the effect of plant harvesting and metal inflow on plant survival. Controlled lab-scale experiments testing native Tasmanian plant species were conducted to discern the key aspects required to implement a phytoextraction system as a part of a treatment train for Fe-rich AMD.

Methods

Experiment setup

Four native plant species were used in the two column studies. *Isolepis inundata, Juncus astreptus,* and *Juncus pallidus* were grown from seed collected in contaminated areas in Tasmania, and *Baloskion tetraphyllum* was purchased from a local Victorian nursery. Columns were constructed of 10 cm diameter, 55 cm tall PVC pipe capped at the base with a threaded outlet. Coarse mesh was placed at the base followed by 600 grams of gravel which was levelled and compacted. Two layers of 1500 grams of sand were then added and were levelled and compacted after each layer. Loose sand was used to fill the rest of the column around the plant, with a small gap left between the top of the column and the top of the sand for the dosing solution.

The dosing solutions used in the plant studies are shown in Table 1 and are based on median metal concentrations for Mt Lyell's Haulage Creek (full-strength AMD) and this median AMD exposed to limestone for 4 h in an oxic environment (pre-treated AMD). Deionised water was also used as a dosing solution for the control. Four replicates of each plant species-and-solution pairing were used in each column study, giving 48 columns in total per study. All columns were dosed twice weekly with 2 L of their appropriate solution and had their stem-heights measured weekly to monitor their health.

After three and a half weeks for establishment in the columns, the first column study ('end-harvest study') began in June 2022. They were dosed with their designated solution for 1 week, topped up with deionised water for 1 week (all columns) as an adjustment period, and then dosed for 5 further weeks with their designated solution. At the end of this dosing period, the plants were harvested and split into their roots and shoots. Shoots were washed thoroughly with deionised water, but roots were washed to keep precipitates intact and remove only metals which weren't sorbed, as this would be more realistic in a phytomining venture. All plant material was dried in the drying oven for weight recording and processing by the ICP-OES.

After 4 weeks of establishment in the columns, the second column study ('mid-harvest study') began in September 2022. They were dosed with their designated solution for 1 week and then all plants were harvested to a height of 10 cm. All harvested plant material was collected for weight recording and metals analysis (shoots_initial). The columns were then topped up with deionised water for two weeks as an adjustment period, and then dosed for a further 5 weeks with their designated solution. At the end of this dosing period, the plants were harvested, split into their shoots (shoots_final) and roots, washed the same way as the end-harvest study, and dried in the drying oven for weight recording and processing by the ICP-OES.

To digest the samples for the ICP-OES, we used a modified EPA method 3050B with smaller acid and hydrogen peroxide volumes (Peña-Icart et al. 2011). Solutions were filtered at 0.45 μm and diluted with deionised water prior to analysis.

Statistical analysis

SPSS V28/29 (IBM Corp 2021) was used for significance testing using linear mixed models within each column study for each element separately. Factors tested were the plant species, the plant section (roots/shoots in the end-harvest study; shoots_initial/shoots_final/roots for the mid-harvest study), and the dosing condition (deionised water/pre-treated AMD/full-strength AMD for both studies; initial pot samples included in end-harvest study). Bonferroni corrections were applied at an $\alpha = 0.05$ level and pairwise post-hoc analyses were undertaken for any significant interactions found in the linear mixed model

***Table 1** Intended dosing solution concentrations in mg/L. pH shown based on experimental results*

	Chemicals used	Pre-treated	Full-strength
Al	$Al_2(SO_4)_3{\cdot}18H_2O$	16	100
Ca	$CaSO_4{\cdot}2H_2O$	350	60
Co	$CoCl_2$	1.1	1.5
Cu	$Cu(SO_4){\cdot}5H_2O$	6	25
Fe	$FeSO_4{\cdot}7H_2O$	350	550
Mg	$MgSO_4{\cdot}7H_2O$	100	100
Mn	$MnSO_4{\cdot}H_2O$	90	100
SO42+	Na_2SO_4	3400	3400
Ni	$NiSO_4{\cdot}6H_2O$	0.22	0.3
Pb	$Pb(NO_3)_2$	0.02	0.06
pH	HCl	4.5	3.1
Sr	$SrCl_2{\cdot}6H_2O$	8	0.6
Zn	$ZnSO_4{\cdot}7H_2O$	3	5

Results

Table 1 shows a summary of which dosing solution provided the highest significant metal uptake based on the marginal means. Further discussion of results will focus on Al and Co, as these two metals have significant implications for this approach. Al was heavily removed during pre-treatment and shows the effect on the higher-concentration elements for phytoextraction. Co remained in the solution during pre-treatment, and is a metal of interest for renewable technologies.

End-harvest study

Al showed no significant difference between species for shoots samples, but showed significantly higher concentrations in *I. inundata* roots. The full-strength AMD also provided the roots with significantly higher Al than the deionised water and initial pots, while the pre-treated AMD was not significantly higher than the deionised water control. No significant differences were seen between dosing solutions in the shoots.

Co showed similar uptake patterns between roots and shoots for each dosing solution in *B. tetraphyllum* plants; what was taken up by the shoots was similar to the concentration around the roots. However, for *I. inundata,* significantly more Co was taken up by pre-treated AMD shoots than full-strength AMD shoots. While the full-strength AMD columns were significantly higher than the controls in Co shoot concentration, much higher concentrations were accumulated in the roots than the shoots. No significant difference was seen between any *J. astreptus* and *J. pallidus* shoot concentrations, even though treated shoots did have higher concentrations than the controls, but Co in *J. astreptus* roots was significantly higher when growing in full-strength AMD compared to other conditions.

Mid-harvest study

The only significant interactions found for Al were between the plant section (roots/shoots) and dosing solution. The full-strength AMD provided significantly higher Al concentrations to the roots, while the pre-treated AMD had the same concentration as the deionised water control. There were no significant differences in the shoots_initial samples, but the full-strength AMD was significantly higher in concentration for the shoots_final samples, and the pre-treated AMD was significantly higher than the deionised water control.

Co showed no significant difference in concentration for the roots and shoots_initial samples, but both the full-strength and pre-treated AMD were significantly higher than the deionised water control in the shoots_final. However, there was no significant difference between the treatments.

The only significant difference between species for Co concentration was that *J. pallidus* had significantly lower shoots_final concentrations than all other species.

Plant survival

Although plants dosed with AMD were able to take up more metals, their health was severely degraded. During the end-harvest study, only *I. inundata* consistently had a positive stem height change in the full-strength AMD, while *B. tetraphyllum* columns dosed with pre-treated AMD remained at a similar height to the deionised water controls. There was not much growth or decline in the end-harvest study, which was conducted in winter.

In the mid-harvest study, *J. pallidus, J. astreptus* and *I. inundata* deionised water columns were able to reach their pre-harvest heights after 5 weeks in the spring conditions,

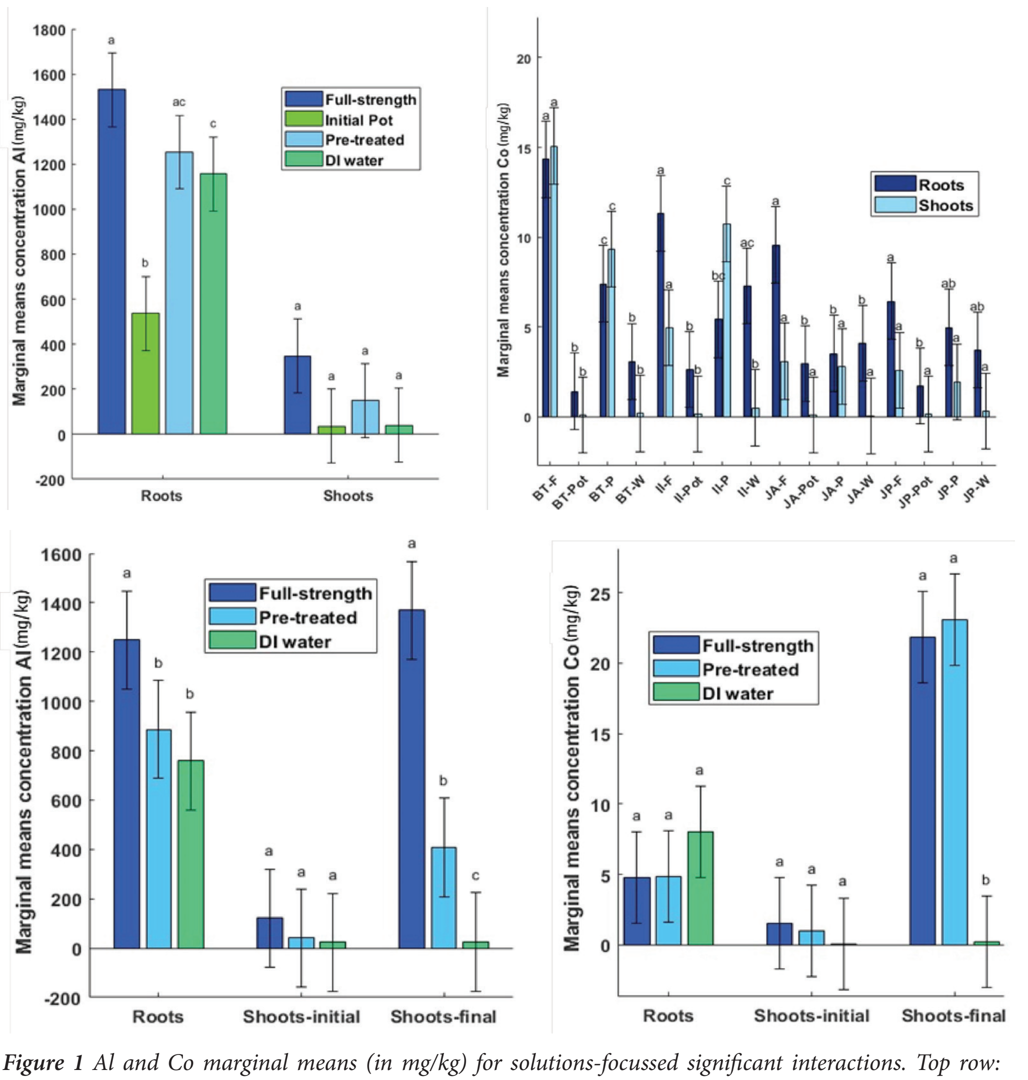

Figure 1 *Al and Co marginal means (in mg/kg) for solutions-focussed significant interactions. Top row: end-harvest study results; bottom row: mid-harvest study results. Marginal means for the same plant section (and within each species for all conditions for end-harvest study Co) followed by a common letter are not significantly different from each other. Significance was tested by a linear mixed model analysis with Bonferroni correction at α = 0.05. Pairwise comparisons are shown only within plant sections and not between species or between separate conditions. Error bars show the 95% confidence interval. W – deionized water; Pot – initial pot; P – pre-treated AMD; F – full-strength AMD*

with *B. tetraphyllum* almost at pre-harvest levels. The pre-treated AMD columns also grew more than the full-strength columns for all but *B. tetraphyllum*, but all columns often grew new shoots rather than regrowing from the cut shoots, leaving a large amount of dead biomass behind at the end of the study.

Discussion

Both studies' results were highly dependent on the plant species, plant section, and metal, with different significant interactions for different metals.

Effects of inflow metal concentrations

The goal of the pre-treatment was to decrease the high concentrations of certain metals in the full-strength AMD (i.e. Fe and Al) to potentially increase the plants' uptake of more economically valuable metals (i.e. Co, Cu, Ni, Zn). Plants grown in environments with lower metal contamination are able to accumulate metals in similar concentrations to those grown in high-metal environments (Deng et al. 2004), but with potentially higher survival rates.

Pre-treatment did not seem to increase the concentration of more economically valuable metals in general. Co most often had significantly higher concentrations in the full-strength AMD across plant species and sections, with only *I. inundata* shoots in the end-harvest study showing higher Co in the pre-treated AMD columns. In the mid-harvest study, there were no significant differences between the treatments for shoots_ final samples for Co. There was, however, a clear species-specific difference in Co uptake in the end-harvest study, with different accumulation trends shown between *B. tetraphyllum* and *I. inundata*. Although these plants are far from Co-hyperaccumulators, any potential recovery of this resource from AMD reduces the reliance on other Co sources, with the potential for ~35 mg of Co per plant (based on the mid-harvest study).

Species comparison

Deionised water columns were the healthiest at the end of the study, indicating that all species were appropriate to be grown in sand in columns in saturated conditions. However, metal uptake was often very species-specific. *I. inundata* often had higher concentrations, while *J. pallidus* often had lower concentrations or the most contrary results to the other species. No plants were identified as hyperaccumulators by traditional or updated measures (van der Ent et al. 2013).

Effects of harvesting mechanism

The magnitude of metals taken up by the plants was similar across both studies, showing that the growing season had less of an influence. This points to an upper limit of metal concentration which is species-specific, but perhaps the speed of metal uptake will depend on the environment.

Conclusions

This project investigated the functional requirements for a phytoextraction system. We found that the two treatment solutions often increased plant metal uptake, but that there was often no significant difference between the full-strength AMD and pre-treated AMD or that the full-strength AMD provided higher metal uptake for the more economic metals. Where the plants stored the metals was species- and metal-specific and could be affected by the dosing solution. Metal accumulation between both studies was similar, but the pre-treated AMD did not decrease the plants' health as severely as the full-strength AMD. While pre-treatment should be considered for plant survival, it may not be necessary to increase plant metal uptake.

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