

Australian Government

Rural Industries Research and Development Corporation

Feasibility of Phytomining

— using plants to extract valuable metals from soils —

by A. T. Harris

November 2008

RIRDC Publication No 07/127 RIRDC Project No PRJ-000543 © 2008 Rural Industries Research and Development Corporation. All rights reserved.

ISBN 1 74151 524 6 ISSN 1440-6845

Feasibility of Phytomining — Using plants to extract valuable metals from soils Publication No. 07/127 Project No. PRJ-000543

The information contained in this publication is intended for general use to assist public knowledge and discussion and to help improve the development of sustainable regions. You must not rely on any information contained in this publication without taking specialist advice relevant to your particular circumstances.

While reasonable care has been taken in preparing this publication to ensure that information is true and correct, the Commonwealth of Australia gives no assurance as to the accuracy of any information in this publication.

The Commonwealth of Australia, the Rural Industries Research and Development Corporation (RIRDC), the authors or contributors expressly disclaim, to the maximum extent permitted by law, all responsibility and liability to any person, arising directly or indirectly from any act or omission, or for any consequences of any such act or omission, made in reliance on the contents of this publication, whether or not caused by any negligence on the part of the Commonwealth of Australia, RIRDC, the authors or contributors.

The Commonwealth of Australia does not necessarily endorse the views in this publication.

This publication is copyright. Apart from any use as permitted under the *Copyright Act 1968*, all other rights are reserved. However, wide dissemination is encouraged. Requests and inquiries concerning reproduction and rights should be addressed to the RIRDC Publications Manager on phone 02 6271 4165.

Researcher Contact Details Dr A.T. Harris Laboratory for Sustainable Technology, School of Chemical and Biomolecular Engineering, University of Sydney, NSW, 2006, AUSTRALIA.

Phone: 02 9351 2926 Fax: 02 9351 2854 Email: a.harris@usyd.edu.au

In submitting this report, the researcher has agreed to RIRDC publishing this material in its edited form.

RIRDC Contact Details

Rural Industries Research and Development Corporation Level 2, 15 National Circuit BARTON ACT 2600 PO Box 4776 KINGSTON ACT 2604

Phone: 02 6271 4100 Fax: 02 6271 4199
Email: rirdc@rirdc.go rirdc@rirdc.gov.au. Web: http://www.rirdc.gov.au

Electronically published in November 2008

Foreword

Australia's rural industries make a fundamental contribution, both to the Australian economy, and our way of life. In addition to the major industries, numerous new and emerging rural industries bring opportunity, diversity and resilience to rural Australia. One of these maybe phytomining, which is the use of plants to harvest valuable metals from soils, sediments and waters.

This report explores the feasibility of phytomining in regional and rural Australia through a desktop study. The aim was to determine particular localities and mineral targets that could support an emerging phytomining industry.

A model is also presented that incorporates economic and scientific data to allow assessment of the likely profitability and sustainability of phytomining in rural Australia.

This project was funded from RIRDC Core Funds which are provided by the Australian Government and is an addition to RIRDC's diverse range of over 1800 research publications. It is part of our New Plant Products R&D program which aims to facilitate the development of new rural industries based on plants or plant products that have commercial potential for Australia.

Most of our publications are available for viewing, downloading or purchasing online through our website:

- downloads at www.rirdc.gov.au/fullreports/index.html
- purchases at www.rirdc.gov.au/eshop

Peter O'Brien Managing Director Rural Industries Research and Development Corporation

Contents

Executive summary

What the report is about

Phytomining is a 'green' approach to the environmentally sensitive and energy intensive practice of mining, involving the use of plants to extract valuable metals from soils, sediments and waters. This is a desktop investigation to assess the feasibility of phytomining. Research suggests that phytomining is an economically and environmentally sustainable technology with possible applications in rural and regional Australia.

Who is the report targeted at?

The target audience for this report is interested researchers and stakeholders in both the mining and agricultural sectors.

Background

Phytomining and phytoremediation involve the extraction of minerals from soils, sediments and waters using specially selected, metal hyperaccumulating plants. Phytomining is commercially motivated, the objective being to produce a viable metal yield, at production costs low enough to compete with traditional mining techniques.

Phytomining is less intrusive than traditional mining techniques, which are energy and resource intensive, and require substantial site remediation at the end-of-life of the mine. By comparison, phytomining:

- 1. Requires reduced energy inputs
- 2. Uses solar energy to generate a 'bio-ore', and
- 3. Improves the quality of the soil for other applications over time.

Depending on the minerals being extracted, and the location, phytomining has an environmental impact similar to a commercial farm. Furthermore, there is potential to develop industrial synergies with related industries. This could come e.g. from the generating of renewable energy during the combustion of the plant biomass during metal recovery, further increasing the profitability of phytomining.

Aims

In this work our aims were:

- 1. To identify appropriate sites for phytomining in Australia, for metals most suited to the phytomining process.
- 2. To provide an insight into the availability of resources at these sites over time.
- 3. To determine which plants are most suited to the identified regions.
- 4. To investigate methods for recovering metals from the plants once sequestered.
- 5. To report a financial and technological model which incorporates metal price, biomass yield, processing cost, mineral yield and concentration gradients.

Methods used

This was a desktop study. While the boundary for this study was Australia wide, analysis was restricted to likely soil compositions and climates for known metal hyperaccumulators, in order to identify the most feasible, near term, phytomining locations. Analysis was also limited to areas where phytomining would most likely be viable, such as sub-economic ore regions, former mine sites, tailings pond irrigation and sewerage sludge disposal areas.

Results/Key findings

We found that, in Australia, the sites most suited to phytomining are those with ultramafic or serpentine soils, which have mineral concentrations too low to be economically mined by traditional means. Ultramafic rocks have high iron and magnesium contents and when weathered produce serpentine soils which generally have low NPK and organic matter, and are shallow and sandy. Phytomining also appears viable where there are high metal concentrations around mine and mineral processing treatment plants (e.g. near tailings dams or smelters). In Australia, it appears that the most promising locations for phytomining generally are in the Western Australian goldfields (gold and nickel) and around Olympic Dam in South Australia (uranium, copper and gold).

Different plants are better at hyper-accumulating different metals, with *Brassica juncea* most appropriate for gold and copper, and *Hybanthus floribundus* suited to nickel phytomining.

Implications for relevant stakeholders for:

Phytomining is largely commercially driven. While there exists an extensive knowledge base of hyperaccumulating plants, phytomining as a concept has only received relatively recent attention due to high metal prices. Further research is required to fully assess the potential of a phytomining industry in Australia.

Recommendations

Our recommendations are as follows:

- 1. Undertake an experimental programme to map the potential areas outlined in this report to determine the metal concentration in the soil. This will lead to a higher degree of certainty as to the potential phytomining yield attainable in these particular regions.
- 2. Undertake an experimental programme to assess the acidity and nutrient availability in these regions. This is especially important when selecting suitable hyperaccumulators. Often nutrients must be added to the soil to obtain a high biomass yield, as well as to neutralise acidic soils. However, depending on the solution used to induce accumulation when gold is concerned, the soil pH requirements differ. This needs to be studied on a case by case basis.
- 3. The specific requirements for irrigation should be determined at each of these locations, and in particular, whether mine tailings are available for this purpose.
- 4. Undertake an experimental programme to assess suitable native hyperaccumulators. One such plant is *Hybanthus floribundus* (Ni)*,* which is naturally occurring in arid areas of Western Australia. These plants may not need irrigation and can be planted on sub-economic nickel feedstocks. However, controlled irrigation for *Brassica juncea* (Au, Cu) and to a lesser extent *Alyssum murale* (Ni) appears necessary to achieve optimum biomass yields.
- 5. Undertake an experimental programme to determine the feasibility of alternating crop rotations as a technique to extract multiple targets from a single site. This may prove to be successful in areas where more than one metal is present and one metal has a lower concentration but a higher return, e.g. gold and copper.

1. Introduction

Phytomining is a 'green' approach to the environmentally sensitive and energy intensive practice of mining, involving the use of plants to extract valuable metals from soils, sediments and waters. Typical feedstocks for a phytomine are either too low in metal content to be productively mined using traditional technologies, or alternatively, too high in metal content such that they hinder the productivity of various horticultural ventures (knowingly or unknowingly) when the main land use is not mining. A related idea is called phytoremediation, which is the treatment of heavy metal contaminated substrates using plants. Contaminated substrates could be found at former industrial sites or industrial waste disposal areas, mine tailings dams and leaching ponds. Plants suited for use in phytomining or remediation have a genetically high tolerance for heavy metals, thought to be either a natural defence mechanism for warding off predators or an evolutionary adaptation to enable a particular plant to survive in naturally high metal environments. Potential 'metal mining' plants are classified as hyperaccumulators, which means they can store particular heavy metals, in large quantities, relative both to their environment and non hyperaccumulating plants.

Phytomining is largely commercially driven. While there exists an extensive knowledge base of hyperaccumulating plants, phytomining as a concept has only received relatively recent attention due to high metal prices.

1.1 Objectives and scope

The overall objective of this project was to determine the feasibility of phytomining in Australia. More specifically, our aims were:

- 1. To identify a range of appropriate sites for phytomining in Australia, for metals most suited to the phytomining process.
- 2. To provide an insight into the availability of mineral resources (i.e. how much metal is available to be recovered) at these sites over time.
- 3. To determine which plants are most suited to the identified regions.
- 4. To investigate methods for recovering metals from the plants once sequestered.
- 5. To highlight a financial and technological model which incorporates metal price, biomass yield, processing cost, mineral yield and concentration gradients.
- 6. Ultimately, to assess the sustainability of phytomining in Australia.

1.2 Study boundaries

While the system boundary for this study was Australia wide, we restricted our analysis to likely soil compositions and climates for known hyperaccumulators, in order to identify the most feasible, near term, phytomining locations. We also constrained our analysis to areas where phytomining would most likely be viable, in the first instance, e.g. sub-economic ore regions, former mine sites, tailings pond irrigation and sewerage sludge disposal areas.

1.3 Key definitions

1.3.1 Phytomining

Phytomining is essentially the generation of revenue by employing a technology that uses plants to mine heavy-metals from otherwise sub-economic ore bodies (Robinson et al., 2002). The main aim of phytomining is to recover these metals for commercial gain (Harris, 2005). Hyper-accumulating plants phytoextract (transport and accumulate), large quantities of metal from particular soils (Li et al., 2003). These plants can then be harvested in the usual way and processed to recover the metals, e.g. via pyrolysis (heating in the absence of oxygen)) or acid digestion and electrowinning. Electrowinning is a method that involves the passing of an electric current through a solution so that the metal is deposited and can then be extracted.

Phytomining has many potential benefits including low cost operation. Therefore there is potential for high returns if the land is managed appropriately, with the right plants selected for the particular soils

in question (Robinson et al., 2002). Often, phytomined land has increased fertility after metals have been extracted. The removal of metals toxic to many plants, and the increased fertility of the land that results from improved management practices, are the two key benefits most often cited by phytomining proponents (Robinson et al., 2002).

Before phytomining is considered at any scale, it must satisfy relevant environmental legislation and be shown to be economically viable. In terms of environmental impacts the fact that it is still a mining venture (as opposed to a farming operation) needs to be weighted against the likely reduction in energy consumption of the mining operation that will result and the potential for biomass electricity generation during metal recovery. The feasibility of a future phytomining industry will ultimately be decided by these economic and environmental considerations.

1.3.2 Hyperaccumulation

Hyperaccumulation, broadly defined, means increased uptake or storage of a particular substance. Some plant species are able to hyperaccumulate certain metals, up to concentrations several hundreds of times those found in non-hyperaccumulating plants. We have identified two common characteristics for hyper-accumulating plants: i) they show a bio-concentration factor greater than one and ii) show hyper-tolerance to metals. The bio-concentration factor is defined as the ratio of the metal concentration in the plant shoots (the most easily obtained and processed part of the plant) to that in the soil. Hyperaccumulator plants generally form organometallic complexes within their cellular system in order to store accumulated metals.

1.3.3 Ultramafic and serpentine soils

Low grade ore which is uneconomic to mine, i.e. the concentration of metal is too low and requires more energy (and other resources) to extract than can be obtained from sales of the metal, is of great interest to phytomining advocates. Indeed there are significantly more low grade ore bodies in Australia than there are proven sites with mining potential. Many of these ore bodies, whether viable or not using existing technology, are associated with ultramafic deposits, i.e. dark soils with high magnesium and iron contents. Ultramafic soils have low organic matter content, are often shallow and sandy and have different vegetation than surrounding soil types (Robinson et al., 1996). These soils, when weathered, produce serpentine soils. Furthermore, they generally contain a high concentration of chromium, magnesium and nickel, low levels of calcium, nitrogen, potassium and phosphorous (essential for most plant growth) and are characterised by a pH of 6-8 (Li et al, 2003).

There have been a number of studies on the incidence of nickel poisoning of plants in serpentine soils. Initially plants begin to grow, but as they develop the soil becomes more acidic and this often hinders or stops further growth. This is due to the increased availability of nickel as the soil becomes more acidic (Robinson et al., 1996). Therefore crops or plantations grown on serpentine soils may be stunted resulting in a lower productivity whilst there remains a high nickel content in the soil.

There are, of course, other soils where metals are present. These include those associated with igneous rock formations as well as granite and other mafic rocks. Metals are also found in sedimentary rock/soil deposits, including the highly valuable gold metal deposits of Western Australia.

2. Common metal hyperaccumulators

The feasibility of phytomining is dependent upon identifying suitable plants species, those which hyperaccumulate specific metals, and then ensuring that these plants are able to grow under the conditions which prevail in the locations where the metals are located. In this section we identify some of the most promising hyperaccumulators reported in the literature. There have been a number of studies on metal hyperaccumulators in the last few decades, however interest in phytomining as a viable land use is comparatively new (due to the changing economic circumstances related to metal supply and demand). In 1999, there were approximately 300 Nickel, 26 Cobalt, 24 Copper, 19 Selenium, 16 Zinc, 11 Manganese, 1 Cadmium and 2 Thalium known hyperaccumulating plants (Anderson et al., 1999). Anderson et al., (1999) has noted the following (Table 1) plant species as having promising hyperaccumulation potential in specific metal rich soils.

Metal element	Species	Concentration (ppm)	Biomass (t/ha)
Cadmium (Cd)	Thlaspi caerulescens	3,000	$\overline{4}$
Cobalt (Co)	Haumaniastrum robertii	10,200	$\overline{4}$
Copper (Cu)	Haumaniastrum katangense	8,356	5
Gold (Au)2	Brassica juncea	10	20
Lead (Pb)	Thlaspi rotundifolium subsp	8,200	$\overline{4}$
Manganese (Mn)	Macadamia neurophylla	55,000	30 9 18
Nickel (Ni)	Alyssum bertolonii	13,400	
Nickel (Ni)	Berkheya coddii	17,000	
Selenium (Se)	Astragalus pattersoni	6,000	5
Thallium (Tl)	Iberis intermedia	3,070	8
Uranium (Ur)	Atriplex confertifolia	100	10
$\text{Zinc}(\text{Zn})$	Thlaspi calaminare	10,000	$\overline{4}$

Table 1: Common metal hyperaccumulators¹, after Anderson et al. (1999).

1. Average values determined from multiple studies

2. Induced hyper-accumulation using ammonium thiocyanate

The specific soil type, nutrient availability, pH and solubility/metal availability all need to be assessed prior to plant selection. Metal ion availability is particularly interesting as some plants can concurrently uptake more than one metal. However, the yield of a particular metal can be reduced as another metal yield increases. In the following sections we review the literature on nickel, copper, gold and uranium uptake using plants. These metals are particularly relevant to Australia given strong market demand and future mining potential.

2.1 Nickel (Ni) hyperaccumulators

Soil pH is a particularly important factor in the uptake and adsorption of metals by plants (Li et al., 2003). A lower pH for the genus *Alyssum* resulted in a lower biomass yield and lower uptake of nickel from the soil. Addition of nitrogen to the soil increased biomass yield but not the uptake of metal. Numerous studies have been conducted on soil and crop management methodologies to enhance the biomass and metal concentration content in the plants to increase phyto-extraction efficiency (summarised by Li et al. 2003).

Alyssum murale is reported to be more robust than *Alyssum corsicum* over a range of soil types, (although in poorly drained soils, plant growth was severely stunted) and has also been shown to withstand extended dry periods. *Alyssum corsicum* phytomining of nickel from contaminated soils around nickel refineries has been proven to yield commercially valuable quantities of nickel (Li et al. 2003). *Alyssum* plants are reported to be best suited to a Mediterranean climate, however in the work

of Li et al (2003) undertaken in a temperate climate, the yield was still a conservative 20t/ha of biomass. *Alyssum* also simultaneously hyperaccumulate cobalt, but to a lesser extent. Li et al (2003) found that on untreated (i.e. not acidified, limed or calcium added) serpentine soils, *Alyssum* had an uptake of approximately 0.8% (8000 ppm) nickel in the biomass (Li et al. 2003). In nickel smelter contaminated soil, including smelter tailings and runoff, the yield increased when the soil was treated with calcium, to between 2.61 to 3.43% in the biomass (Li et al. 2003). *Alyssum bertolonii* (Table 1) is of the same genus as *A. murale* and *A. corsicum*.

Hybanthus floribundus was reported to hyperaccumulate nickel to over 1% dry biomass and over 23% in the ash when incinerated (Severne and Brooks, 1971). This plant was investigated for application in the Eastern Gold fields of Western Australia because it grows readily in arid conditions and high metal content soils. The soil had an average metal content of 670 ppm, and a cobalt content of 70 ppm. The *Hybanthus floribundus* ash content when incinerated contained over 100,000 ppm nickel and 600 ppm cobalt (Severne and Brooks, 1971). However the plant was found to have no affinity for copper.

One comparatively rare native which grows readily on serpentine soils, in particular in the Rockhampton area of Queensland, is *Stackhousia tryonii*. *S tryonii* has been reported to hyperaccumulate nickel up to 4% in leaf dry weight, or 41,300 ppm dry mass (Ashwath et al., 2003). The downside is that it grows comparatively slowly, although there are plans to isolate the genes that form organo-metallic complexes inside the plant and insert these into faster growing and higher biomass yielding plants (Bhatia, 2005). At present, it is uneconomic to use *Stackhousia tryonii* for a phytomining venture because of its slow growth rate.

Research by Robinson et al. (1998) found that an average concentration of nickel in ultramafic soils in New Caledonia, Spain, Morocco, Firenze and New Zealand was ~2000 ppm (0.2%). Between 13 to 80% of this nickel was available to plants, largely dependent on the acidity of the soil. This suggests that by amending the soil pH metal uptake can be enhanced.

2.2 Copper (Cu) hyperaccumulators

In addition to *Haumaniastrum katangense* reported in Table 1, *Becium homblei* is known to hyperaccumulate copper, yielding up to 6,300 ppm in the ash of plants grown in copper rich soils (Severne and Brooks, 1972)*. Brassica juncea* was reported by Anderson et al., (2005) to hyperaccumulate 541 ppm at the same time as accumulating a significant quantity of gold. As many copper mines in Australia also have appreciable concentrations of gold in their ore (e.g. Olympic Dam in South Australia), *Brassica juncea* shows significant potential. However Anderson et al., (2005) used a NaCN soil treatment to induce metal uptake. This approach is known as induced hyperaccumulation, and while successful, is considerably more expensive than traditional phytomining.

2.3 Gold (Au) hyperaccumulators

Given the record spot price for gold, there is a large incentive to identify plants suitable for gold phytomining. To date however, no natural hyperaccumulators for gold have been identified. A number of studies have looked at induced hyperaccumulation, involving the addition of a complexing solution to the soil (Anderson et al., 1999 and 2005). The complexing solution most beneficial for gold accumulation in *Brassica juncea* (selected because of its high biomass yield) was thiocyanate (SCN⁻) (Anderson et al.. 1999, Anderson et al., 2005, Msuya et al., 1999). Thiocyanate is particularly useful when applied to acidic and neutral soils but results in low productivity in alkaline soils (Anderson et al., 2005).

Brassica junea yields approximately 10-15 t/ha of biomass following a ten week growth cycle. Alkaline growth conditions, that is on soils treated with calcium (as CaOH), resulted in the decline of plant health and lower yields, however this was observed to stabilise the Au-SCN complex (Anderson et al., 2005), and so is potentially advantageous from an environmental perspective. In basic soils NaSCN has been shown to be useful, typically at an application rate of 0.15g/kg soil at a solution concentration of 1.4g/L of CN- (Anderson et al., 2005). At higher levels, *Brassica juncea* produced 39 ppm Au and 541 ppm Cu when treated with NaSCN at 0.6mg/kg soil. This experiment was undertaken using a soil with a gold concentration of 0.64 ppm (Anderson et al, 2005) and the *Brassica juncea*

accumulated 18% of the gold present in the substrate (Anderson et al., 2005). This work was performed at a gold mine in Brazil, where there are well defined dry and wet seasons and the average annual rainfall is 600mm.

There are many possible locations suited to the phytomining of gold in Australia. The most promising of these contain comparatively high concentrations of gold close to the surface (and therefore accessible to plant roots), e.g. in tailings ponds and heap leach windrows. Because the most effective technique for gold phytomining is induced accumulation, the exact plant species is no longer the most important variable. Hence plants which easily and quickly grow on mine tailings may be used, e.g. *Chicory*. Furthermore, Anderson et al. (1998) confirmed that residual thiocyanate is easily broken down in the substrate. A further aspect of phytomining for gold is that induced hyper-accumulation can also be used to remediate contaminated mine sites. In this case the yield of gold will potentially cover the cost of the venture, and in some cases, generate a profit.

The steps for phytomining with gold, reported by Anderson et al., (2004) are as follows:

- 1. Identify a suitable former gold mine or soil identified as auriferous (i.e. containing gold).
- 2. Plant a species that is tolerant to the local conditions, e.g. can grow in high mineral content soils, is fast growing and has a large biomass yield.
- 3. As plants near maturity, treat the soil with an appropriate inducer this causes a pulse of metal to be released into the soil, which is then accumulated by the plants.
- 4. When plants show signs of poor health, i.e. metal shock, they can be harvested.
- 5. Recover the gold from the biomass.

2.4 Uranium (U) hyperaccumulators

In addition to *Atriplex confertifolia* (identified in Table 1), *Uncinia leptostachya* is also known to hyperaccumulate uranium, yielding up to 25,000 ppm in the ash of incinerated plants (Severne and Brooks, 1972). As with other metals, in the first instance, uranium phytomining would most likely occur in the region of tailings ponds as a form of remediation. We note however that further fundamental research is required in this case as there is little published work on the phytomining of radionuclides. Further research is also required to investigate the ability of the proposed plants to grow on soils with a variety of metals as well as to determine their growth rate and biomass yield under these conditions. Alternate crop rotations may be viable in this case.

2.5 Summary of Ni, Cu, Au and U hyperaccumulators

Table 2 is a summary of the plants most suited to phytomining nickel, gold, copper and uranium under typical Australian conditions.

Table 2: Summary of phytomining plants for particular metals and their yields.

1. n/a is due to slow growth and biomass yield, however genetic engineering of growth rates may have potential.

2. Mediterranean has some similarities to climates in Australia, particularly in the south of WA and SA.

3. Desert shrub has excellent potential in the Eastern goldfields areas of WA, central and SA, central QLD.

4. This plant has proven to be able to grow in most areas with the aid of small quantitites of fertilisers and irrigation, given that gold hyper-accumulation needs to be induced, irrigation is necessary in any event.

3. Potential phytomining opportunities in Australia

Heavy metal emissions from metal smelters and refineries often accumulate in nearby soils. In the first instance, these locations would be prime candidates for a practical demonstration of the potential of phytomining in Australia. Mine sites with tailings ponds requiring remediation also make good candidates, as do sites treated with sewage sludge containing high concentrations of heavy metals (Li et al. 2003). A large proportion of soils in Australia are ultramafic. Whilst ultramafic soils often have a high nickel content the majority have been classified as sub economic and are therefore appropriate for phytomining. In the remainder of this section we identify specific locations within rural and regional Australia that would benefit from a more detail investigation of phytomining potential.

3.1 Phytomining opportunities in the vicinity of existing mines

90% of the known nickel mineral deposits in Australia are located in Western Australia (Australian Mineral Atlas, 2006). 8.9% of these resources are classified as sub-economic, i.e. mining the ore is not profitable using existing technology. We contend that these sub-economic deposits show promise for a field demonstration of phytomining.

The Nickel mineral deposits in WA are largely associated with the Eastern Goldfields area near Kalgoorlie. As plants suited to this environment have been investigated previously for phytomining potential, e.g. *Hybanthus floribundus* and *Alyssum murale*, it is plausible that a trial could be implemented in the near future. Known nickel mineral deposits in Australia are shown in Figure 1. In addition to deposits in WA, there are opportunities in Qld, NSW and Tasmania, particularly related to the treatment of tailings residues. This approach is likely to be considerably less energy intensive than solvent extraction/electrowinning, the standard approach. There is also potential for irrigating crops with tailings liquor and dosing with solution in areas around tailings ponds.

The soils of the known nickel deposits of Western Australia are largely derived from granites but also have ultramafic, mafic volcanic and felsic rocks running through the granite. This makes the soil ideal for both nickel and gold, as well as other metals including magnesium and iron.

Gold deposits however, are found over a larger area of Australia (Figure 2). Gold deposits are found in ultramafic soils but more commonly in auriferous soils which are interspersed throughout the volcanic and granite layers and even in some sedimentary rock deposits. In short, there is a larger mineral occurrence, but also a larger sub-economic mineral occurrence, given the low concentration and the cost of extraction.

Much of the gold is co-located with iron oxide supported copper or with some uranium, such as the Olympic Dam and Tennant Creek mines in South Australia and the Northern Territory. There are about 107 Mt of sub marginal deposits located in WA (Australian Mineral Atlas, 2006). We contend that, in the majority of cases, these could be phytomined concurrently for gold and nickel (and other metals) via induced accumulation, so long as precautions to prevent ground water contamination are observed.

Figure 2: Gold mineral deposits in Australia. Again the eastern goldfields region of WA is highlighted.

In some cases it would be possible to recover copper in addition to nickel and gold, because copper is observed in many of the soils where these other metals are found. Approximately 4.9Mt of subeconomic copper deposits (Figure 3) have been identified in Australia that could potentially be viable locations for a copper phytomine (Australian Mineral Atlas, 2006). However we feel that copper phytomining would be most viable when supplementing gold, nickel or uranium phytomining. Specific crops could be alternated with intermittent solution dosing if the copper concentration was high: i.e. one crop would be used to recover gold and then an alternate crop to recover copper e.g. *Haumaniastrum katangense.*

Copper mineral deposits

Figure 3: Known copper deposits in Australia.

Occurrences of uranium are not as common as other metal deposits in Australia, but it is nevertheless, a potentially valuable phytomining target. Again most uranium is associated with gold and copper, and hence a phytomine recovering all of these, using a rotating crop scheme, would be most feasible.

Uranium mineral deposits

Mineral deposit

Figure 4: Known uranium deposits in Australia.

3.2 Refinery and smelter phytomining

Major mineral processing centres in Australia are highlighted in Figure 5. A Nickel smelter exists in Kalgoorlie, WA and two nickel refineries exist, one in Kwinana, WA, and one in Yabulu near Townsville, QLD. Major copper smelters are located at Mt Isa, QLD and Olympic Dam, SA. There are copper refineries located in Townsville, Olympic Dam and Port Pirie, SA. All of these processing centres have been in operation for some time and hence there is potential to address issues of metal contamination at many of these sites, using a phytoremediation approach.

3.3 Sewerage sludge phytomining

Sewerage sludge typically has both a high metal and high nutrient content (e.g. N, P and K), which is potentially advantageous for phytomining. Furthermore sewerage sludge deposits in Australia are often stockpiled and potential uses include ash to be locked into cement or as landfill for freeway construction (Melbourne Water, 2006). The phytomining potential from sewerage could be realised by irrigating low value land with a sludge solution; however this requires further investigation, particularly in relation to public health. Sewerage sludge is largely seen as a phytoremediation venture rather than a phytomining venture, however there are resources in Australia, most notably at Werribee in Victoria, where sewage sludge has been stockpiled for many years and a large, metal rich resource has developed as a result.

Figure 5: Mineral processing centres throughout Australia where there is potential for phytomining.

4. Metal recovery from plants

There are essentially two techniques to process biomass containing metal. The first is via high temperature pyrolysis or combustion followed by smelting the ash. This approach is attractive because there exists the possibility to use the energy generated during combustion to produce electricity. The second is through acid digestion of the plant matter and further processing, such as electrowinning or solvent extraction to recover the metal. Insufficient research has been undertaken to determine which is the most feasible alternative, in relation to specific hyperaccumulating plants, metals, ore bodies or phytomining locations.

There have however been several investigations into the extraction of metal from plants. While Koppulu et al. (2003) published a series of papers on the separation of metals via pyrolysis (heating in the absence of oxygen), most research has focussed on the combustion (incineration) of the biomass to generate energy and recover a concentrated bio-ore, which can then be smelted. This is the most likely, near term, pathway for recovering the metals. Figure 6 from Brooks et al. (1998) shows a model for an economically feasible phytomining operation, including metal recovery.

Figure 6: Phytomining model (Brooks et al., 1998).

5. Assessing the economic feasibility of phytomining

5.1 Technology approach

The technology approach upon which the subsequent economic model will be based involves the combustion of harvested biomass to generate electricity and create a bio-ore, which can be stored and processed when metal prices are favourable (Figure 7, Anderson et al., 1999).

Figure 7: Technology approach for phytomining (Anderson et al., 1999)

This particular approach was selected as it involves biomass processing technologies which are proven and which enhance opportunities for the sale of by-products (e.g. energy), which increase the overall profitability.

5.2 Economic model for phytomining assessment¹

Robinson et al (2003) proposed the following model to evaluate the economic viability of a phytoextration process:

$$
V = A \int_{0}^{t} (C1 + C2 - P1 \times V1 - P2 \times V2) dt + \sum_{x=1,...,t} \int_{0}^{x} (C1 + C2 - P1 \times V1 - P2 \times V2) dt \times \frac{l}{100} \tag{1}
$$

where: V is the cost of phytoextration $(\$)$

- *A* is the total area (ha)
- *C*1 is the cost of planting (\$/ha)
*C*2 is the cost of production (\$/h
- *C*2 is the cost of production (\$/ha)
*P*1 is the production of saleable bio
- *P*1 is the production of saleable biomass (t/ha) $V1$ is the value of the biomass (\$/t)
- *V*1 is the value of the biomass $(\frac{f}{f})$
*P*2 is the production of the bio-ore
- *P*2 is the production of the bio-ore (t/ha)
*V*2 is the value of the bio-ore $(\frac{f}{h})$
- is the value of the bio-ore $(\frac{f}{f})$
- *l* is the interest rate $(\%)$

The first step requires an examination of the cost of planting as a function of time. The cost of planting can be expressed as the combination of the cost of mechanical site preparation and the cost of seeding. For this analysis we assumed that deep ripping and cultivation was used as the mechanical preparation method (this is the most common approach at commercial plantations) and mouldboard seeding as the method of direct seeding. These have associated costs of 124 \$/ha and 1,326 \$/ha (seeds inclusive) respectively. This gives:

 $C1 = 1450h$ (2)

1

where: *h* is the number of harvests per annum

Now considering the cost of production we combine the cost of monitoring (30 \$/ha), the cost of fertilizing/chemical spray (90 \$/ha) and the cost of chemicals used to induce hyper-accumulation as required to give:

$$
C2 = 30 + 90s + C_{chem} \tag{3}
$$

where: s is the number of fertilizer/chemical applications per annum C_{chem} is the cost of chemicals for induced hyper-accumulation is the cost of chemicals for induced hyper-accumulation

In the technology model the biomass is burnt to generate electricity for the grid with the amount of biomass production per hectare being specified by the species of plant utilized for phytomining. Table 3 outlines the characteristics of the various species studied in this work.

 1 The model equations reported in this section are reproduced from Robinson et al., 2003.

Element	Species	Mean metal concentration (mg/kg.d.w)	Dry Biomass (t/ha)	Metal cost (AU\$/kg)
Au (induced)	Brassica juncea	10	20	20,153.00
Cu	Haumaniastrum katangense	8,356		9.41
Ni	Alyssum bertolonii	13,400		42.64
	Berkheya codii	17,000	22	
Tl	Biscutella laevigata	13,768		336.00
	Iberis intermedia	4,055	10	
U	Atriplex confertifolia	100		25.95

Table 3: Species characteristics for phytomining

The value of the biomass is based on the energy obtained from burning it, which we have assumed as having the equivalent heat of combustion of dry wood giving 15,500 MJ/(t dry mass). Using a conversion efficiency of 36% and average profit of 0.05 \$/kW.hr we can calculate the value of the biomass as follows:

$$
V1 = 215 \, (\$/t) \tag{4}
$$

Finally we can couple the production rate of bio-ore and the value of the bio-ore, eliminating unknowns by assuming that the mean metal concentration is equivalent to the quantity of metal obtained from the bio-ore. However this does not account for the metal concentration gradient so we must first consider the change in soil concentration at depth z (Robinson et al., 2003):

$$
\Delta \big[M\big]_{z} = \frac{1}{\rho_z} \int_{0}^{t} R_z T C \phi dt \tag{5}
$$

where: $\Delta[M]_{z}$ is the in soil solution metal concentration at depth z (mg/kg)

Assuming a linear relationship between soil solution metal concentration and the plant uptake of the metal, an efficiency factor ε may be introduced to express the changes in metal concentration gradient on the metal concentration in the harvested biomass where:

$$
\varepsilon = \frac{C_t}{C_0} \tag{6}
$$

where: C_0 is the initial metal concentration in the soil solution before phytomining (mg/kg)
 C_i is the current metal concentration in the soil solution (mg/kg) is the current metal concentration in the soil solution (mg/kg)

The value of C_t can be determined by integration of equation (5) with respect to z assuming homogenous metal distribution over the depth of the plants root system. This gives:

$$
C_t = C_0 - \frac{T C_0 \phi}{\rho_{mean}} dt
$$
\n(7)

Equation (7) may be substituted into equation (6) to give the efficiency factor as follows:

$$
\varepsilon = 1 - \frac{T\phi t}{p_{mean}}\tag{8}
$$

The value and production of the bio-ore can now be expressed by utilising the efficiency factor as follows:

$$
C3 = P2 \times C2 = 1000 \times \varepsilon \times C_{metal} \times M_{biomass} \times V_{metal}
$$
\n(9)

where: C_{metal} is the metal conc (kg/(kg dry biomass) at a soil solution metal conc of C_0 M_{biomass} is the dry mass of the biomass (t/ha) V_{metal} is the price of the metal (\$/kg)

Compiling each of the functions expressed in equations (2) to (9) gives the following component cost function:

$$
f(t) = \int_{0}^{t} (1450h) + (30 + 90s + C_{chem}) - 215P1 - 1000\epsilon C_{metal} \times M_{biomass} \times V_{metal}
$$

Assuming an annual harvest and a biannual application of fertilizer/herbicides this function is simplified, and can be integrated with respect to time, to give:

$$
f(t) = \left[\left(1660C_{chem} - 215P1 - 1000 \left(1 - \frac{T\phi}{p_{mean}} \right) C_{metal} M_{biomass} V_{metal} \right) t \right]_0^t
$$
 (10)

6. Economic and environmental feasibility

Phytomining is inherently more sustainable than traditional mining processes, in that it requires fewer resource and energy inputs. We assume that markets exist (and will continue to exist) for minerals currently being extracted using traditional mining approaches, and that this will continue indefinitely until a more environmentally acceptable extraction route is identified, which offers considerable benefits without compromising economic viability. Traditional mining approaches can potentially be highly destructive and intrusive to natural systems, and mineral extraction by this means is resource and energy intensive. It involves the extraction of ore from the earth's crust using heavy machinery, ore crushing and concentration. The minerals are extracted by methods including smelting at high temperatures or solvent extraction or electrowinning. By comparison, phytomining requires the farming of plants in soils with high mineral content. The plants require chemical treatments, such as fertilisers, and regular irrigation, however, unless a chelating agent is required, the environmental impacts of this stage of production are no worse than a commercial farm. Phytomining employs solar energy, a renewable resource, to generate a bio-ore, which is then harvested and the minerals are extracted by a similar method to those used in traditional mining. Sites that have been phytomined have lower mineral contents in their soils, and can therefore be used for a wider range of applications (including farming). By contrast, at the end of the useful lifetime of a traditional mine, considerable effort must be made to remediate the site, using techniques such as revegetation.

In addition to requiring less energy and resources, and being less intrusive, phytomining also offers the potential for the establishment of industrial ecologies, particularly through the generation of electricity. This scenario is possible if the biomass is burned to produce a mineral-rich ash for smelting. This electricity would be considered "greenhouse neutral" in that it has no net effect on atmospheric carbon dioxide concentrations. It is highly desirable to establish industrial synergies, since they reduce the volume of waste requiring treatment, and have a higher overall mass and energy efficiency than can be achieved separately. This is particularly true because it would increase the economic feasibility of the phytomining facility, and promote another sustainable technology. A study undertaken by Li et al (2003) found that although the biomass electricity generation was intermittent, it produced \sim US\$131 per hectare. When combined with seasonally varying crops and other matter suitable for biomass electricity generation to fill in the period when the phyto-extracting crop was not able to be processed, there is the potential for this to further increase profits and to further aid the environment.

Phytomining is more sustainable than the extraction of primary mineral resources by traditional means. Phytomining could further reduce the environmental impact of mining if it were employed in conjunction with increased material recovery and recycling from scrap metal sources. Waste metal requires very little energy input compared with the smelting process. Demand for traditionally extracted metals, and the associated environmental consequences, could be further reduced if a greater proportion of scrap metals (such as copper and nickel) were reused. This would most likely involve the development of novel waste separation methods.

The technological and economic models described in Section 5 were used to assess the viability of phytomining in Australia. Using sample data (actual examples of metallic concentrations in soils were unavailable) it was found that the annual revenue that could be realised using phytomining is in the region of \$540,000/ha. These calculations take into account annual costs, such as planting crops, irrigation and harvesting, however, they do not include any estimate of the capital costs of the site. At low soil concentrations, which would be experienced after several years of phytomining, the venture would no longer be viable, and a profit could no longer be realised. At this point, the land would have effectively been phytoremediated, and could be used for another application.

7. Conclusions and recommendations

Phytomining is both economically and environmentally feasible, and provided that resources such as water and fertiliser are available in locations with suitable soils, it should be explored further. Our recommendations are as follows.

- 1. Undertake an experimental programme to map the potential areas outlined in this report to determine the metal concentration in the soil. This will lead to a higher degree of certainty as to the potential phytomining yield attainable in these particular regions.
- 2. Undertake an experimental programme to assess the acidity and nutrient availability in these regions. This is especially important when selecting suitable hyperaccumulators. Often nutrients must be added to the soil to obtain a high biomass yield, as well as to neutralise acidic soils. However, depending on the solution used to induce accumulation when gold is concerned, the soil pH requirements differ. This needs to be studied on a case by case basis.
- 3. The specific requirements for irrigation should be determined at each of these locations,, and in particular whether mine tailings are available for this purpose.
- 4. Undertake an experimental programme to assess the suitable of native hyperaccumulators, e.g. *Hybanthus floribundus* (Ni)*,* which are naturally occurring in arid areas of Western Australia. These plants may not need irrigation and can be planted on sub-economic nickel feedstocks, whereas controlled irrigation for *Brassica juncea* (Au, Cu) and to a lesser extent *Alyssum murale* (Ni) appears to be necessary to achieve optimum biomass yields.
- 5. Undertake an experimental programme to determine the feasibility of alternating crop rotations as a technique to extract multiple targets from a single site. This may prove to be successful in areas where more than one metal is present and one metal has a lower concentration but a higher return, e.g. gold and copper.

In each case above we recommend the collaboration of the mining and agricultural sectors.

References

Anderson, C. N., Brooks, R. R., Chiarucci, C. J., Leblanc, M., Robinson, B. H., Simcock, R., and Stewart, R. B., (1999), 'Phytomining for nickel, thallium and gold', *Journal of Geochemical Exploration,* 67, pp407-415.

Anderson, C. N. W., Stewart, R. B., Moreno, F., Wressman, C. T. J., Gardea-Torresday, J. L., Robinson, B. H., and Meech, J. A., (2004), 'Gold phytomining. Novel developments in a plant based mining system', Published in *Proceedings of the Gold 2003 Conference: New Industrial Applications of Gold*. pp. 35-45.

Anderson, C. N., Brooks, R. R., Stewart, R. B., and Simcock, R., (1998), 'Harvesting a crop of gold in plants', *Nature,* Vol. 395, pp554.

Anderson, C., Moreno, F., and Meech, J., (2005), 'A field demonstration of gold phytoextraction technology', *Minerals Engineering',* 18, pp385-392.

Ashwath, N., (2003), 'Localization of nickel in Australian Ni-hyperaccumulating plant Stackhousia tryonii using PIXE & SIMS', *AINSE Progress Report*, pp1-3.

Australian Mine Atlas, accessed 5th November 2006, http://www.australianminesatlas.gov.au.

Bhatia, N., (2005) , 'Mining with metal munchers', accessed on the $5th$ November 2006, http://velocity.ansto.gov.au/velocity/ans0006/article_01.asp.

Brooks RR, Chambers MF, Nicks LJ, Robinson BH (1998). Phytomining. Trends in Plant Science 3(9), 359-362.

Brooks, B. H., Gregg, P. E. H., and Kirkman, J. H., (1998), 'The nickel phytoextraction potential of some ultramafic soils as determined by sequential extraction', *Geoderma,* 87, pp293-304.

Brooks RR, Anderson C, Stewart RB, Robinson BH (1999). Phytomining: growing a crop of a metal. Biologist 46(5), 201-205.

Harris, A., (2005), 'The future of mining', *The Chemical Engineer'*, May 2005, pp40-41.

Koppolu, L., and Clements, L. D., (2003), 'Pyrolysis as a technique for separating heavy metals from hyper accumulator biomass', *Biomass and bioenergy,* 24, pp69-79.

Koppolu, L., Foster, A. A., and Clements, L. D., (2003), 'Pyrolysis as a technique for separating heavy metals from hyperaccumulators,. Part II: Lab-scale pyrolysis of synthetic hyperaccumulator biomass', *Biomass and energy',* 25, pp651-663.

Koppulu, L., Ramakrishna, P., and Clements, L. D., (2004), 'Pyrolysis as a technique for separating heavy metals from hyperaccumulators. Part III: pilot scale pyrolysis of synthetic hyperaccumulator biomass', *Biomass and bioenergy,* 26, pp463-472.

Li, Y. M., Chaney, R., Brewer, E., Roseburg, R., Angle, S., Baker, A., Reeves, R., and Nelkin, J., (2002), 'Development of a technology for commercial phytoextraction of nickel: economic and technical considerations', *Plant and soil,* 249, pp107-115.

Li, Y. M., Chaney, R., Angle, S., Brown, S. L., Baker, A., Roseburg, R. J., Reeves, R., Ryan, J. A., McKenna, M. A., and Kukier, U., (2003), 'Commercialization of phyto-extraction and phytostabilization of metal rich soils', USDA-Agricultural Research Service Viridian Environmental LLC, Houston, Texas, USA, accessed on the 5th November 2006, http://www.cluin.org/studio/2003phyto/prez/41.pdf.

Melbourne water, (2006), 'Sustainable resource management – biosolids', accessed on $5th$ Nov 2006, http://www.melbournewater.com.au/content/publications/fact_sheets/sewerage/biosolids.asp?bhfv=6& bhsh=768&bhsw=1024&bhqs=1.

Msuya, F. A., Brooks, R. R., and Anderson, C. N., (1999), 'Chemically-induced uptake of gold by root crops: Its significance for phytomining', *Gold Bulletin,* Vol. 33, No. 4, pp134-137.

Prasad, M. N. V., (2002), 'Phytoremediation of metal-polluted ecosystems: Hype for commercialization', *Russian Journal of plant physiology',* Vol. 50, No. 5, pp686-700. Reeves, R., (2003), 'Tropical and hyperaccumulators of metals and their potential for phytoextraction', *Plant and soil',* 249, pp57-65.

Robinson, B., Brooks, R., Kirkman, J., Grgg, P., and Gremigni, P., (1996), ''Plant-available elements in soils and their influence on the vegetation over ultramafic (serpentine) rocks in New Zealand', *Journal of the Royal Sociaty of New Zealand,* Vol. 26, No. 4, pp457-468.

Robinson, B., Fernandez, J. F., Madejon, P., Maranon, T., Murillo, J. M., Green, S., and Clothier, B., (2003), 'Phytoextraction: an assessment of biogeochemical and economic viability', *Plant and Soil,* 249, pp117-125.

Schirmer, J, Field, J; Cost of Revegetation Final Report; ANU Forestry, Greening Australia,l 2000

Serverne, B. C., and Brooks, R. R., (1971), 'A Nickel accumulating plant from Western Australia', *Planta*, Vol. 103, pp 91-94.