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Phytomining for nickel, thallium and gold

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Abstract

The technique of phytomining involves growing a crop of a metal-hyperaccumulating plant species, harvesting the biomass and burning it to produce a bio-ore. The first phytomining experiments were carried out in California using the Ni-hyperaccumulator *Streptanthus polygaloides* and it was found that a yield of 100 kg/ha of sulphur-free Ni could be produced. We have used the same technique to test the phytomining potential of the Ni-hyperaccumulators *Alyssum bertolonii* from Italy and *Berkheya coddii* from South Africa. The effect of different fertiliser treatments on growth of *Alyssum bertolonii* was established in situ in Tuscany and showed that the biomass of the plant could be increased by a factor of nearly 3 (4.5 t/ha to 12 t/ha) without significant loss of the Ni concentration (7600 mg/kg) in the plant. Analogous experiments have been carried out on *Berkheya coddii* where a biomass yield of over 20 t/ha can readily be achieved though the Ni concentration is not as high as in *A. bertolonii*. The total yield is, however, much greater. We have also been able to induce plants to hyperaccumulate Au by adding ammonium thiocyanate to the substrate. Up to 57 mg/kg Au (dry mass) could be accumulated by Indian mustard (*Brassica juncea*). Unusual hyperaccumulation (>500 mg/kg dry mass) of Tl has been determined in *Iberis intermedia* and *Biscutella laevigata* (Brassicaceae) from southern France. The *Iberis* contained up to 0.4% Tl (4000 mg/kg) in the whole-plant dry matter and the *Biscutella* over 1.5%. This unusually high accumulation of Tl has significance for animal and human health, phytoremediation of contaminated soils, and phytomining for Tl. We calculate that using *Iberis*, a net return of $ US 1200/ha (twice the return from a crop of wheat) would be possible with a biomass yield of 10 t/ha containing 0.08% Tl in dry matter. The break-even point (net yield of $ US 500/ha) would require 170 mg/kg (0.017%) Tl in dry matter. A model of a phytomining operation and its economics is presented and its advantages and disadvantages discussed.

Keywords: *Alyssum bertolonii*; *Berkheya coddi*; phytomining; phytoremediation; gold; nickel; thallium

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1. Introduction

The technique of *phytomining* involves the use of *hyperaccumulator plants* to grow and concentrate a metal. Subsequently, the crop is harvested and the metal extracted. Hyperaccumulator plants were originally defined by Brooks et al. (1977) as taxa containing >1000 mg/kg (ppm) Ni in their dry biomass. This concentration was selected on the basis of being 100 times the Ni concentration of non-accumulator

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plants, even when growing over Ni-rich ultramafic ('serpentine') soils. The term hyperaccumulator was later redefined to include uptake by plants of most other heavy metals except for Cd (at a threshold of 100 mg/kg — Reeves et al., 1995), Mn and Zn (at 10,000 mg/kg — Reeves and Brooks, 1983), and Au (at 1 mg/kg — Anderson et al., 1998).

There are about 300 Ni-hyperaccumulator species, 26 of Co, 24 of Cu, 19 of Se, 16 of Zn, 11 of Mn, 2 of Tl (including new data in this present paper) and one of Cd (Table 1). Most of these plants were initially regarded as scientific curiosities until it was proposed by Chaney (1983) and Baker and Brooks (1989) that they might be used to remove pollutants from soils (*phytoremediation*). Their use for phytomining was first suggested by Chaney (1983). A phytomining operation would entail planting a hyperaccumulator crop over a low-grade ore body or mineralized soil, followed by harvesting and incineration of the biomass to produce a commercial *bio-ore*. A U.S. Patent has since been taken out on phytomining for various metals including Ni (Chaney et al., 1998).

2. Phytomining for nickel

2.1. Pioneering studies with Streptanthus polygaloides

The first field trials on Ni phytomining in 1994 were based at the US Bureau of Mines, Reno, Nevada (Nicks and Chambers, 1995, 1998) and used a naturally occurring stand of *Streptanthus polygaloides* (Fig. 1), a known Ni-hyperaccumulator (Reeves et al., 1981). The soil contained about 0.35% Ni, well below the economic range for conventional mining. Nicks and Chambers (1995, 1998) proposed that a net return to the grower of \$ US 513/ha could be achieved, assuming that: (1) a minimum of selective breeding produced plants with 1% Ni in dry mass; (2) the world price of Ni was \$ US 7.65/kg; (3) the biomass yield after moderate fertilization was 10 t/ha; (4) a quarter of the energy of combustion of the biomass could be turned into electricity for a yield of \$ US 131/ha; (5) the return to the grower would be half of the gross yield of \$ US 765 for the metal plus the energy yield of \$ US 131. This compares well with the average returns from other crops — for example, it is well in excess of the average return of \$ US 333/ha (including \$ US 111 for wheat straw) obtained by US wheat farmers in 1995.

Fig. 1. A crop of nickel in plants of *Streptanthus polygaloides* growing in California. Photo by Larry Nicks and Michael Chambers.

2.2. Studies with Alyssum bertolonii

Alyssum bertolonii (Fig. 2), the first plant species identified as a hyperaccumulator of Ni (Minguzzi and Vergnano, 1948) was used in the second phytomining field trials (Robinson et al., 1997a) in Italy at Murlo, Tuscany. Plants were fertilized with N + P + K combinations over a two-year period. A threefold increase of the biomass of dry matter to 9.0 t/ha was gained with N + P + K without dilution of the unfertilized Ni concentration. A Ni level of 0.8% in dry matter (11% in ash), equated to a yield of 72

Table 1
Specific hyperaccumulators (natural and induced) that could be used for phytomining

Element	Species	Mean metal concn. (mg/kg d.w.)	Biomass (t/ha)
Cadmium	*Thlaspi caerulescens*	3,000 (1)	4
Cobalt	*Haumaniastrum robertii*	10,200 (1)	4
Copper	*Haumaniastrum katangense*	8,356 (1)	5
Gold [a]	*Brassica juncea*	10 (0.001)	20
Lead	*Thlaspi rotundifolium* subsp.	8,200 (5)	4
Manganese	*Macadamia neurophylla*	55,000 (400)	30
Nickel	*Alyssum bertolonii*	13,400 (2)	9
	Berkheya coddii	17,000 (2)	22
Selenium	*Astragalus pattersoni*	6,000 (1)	5
Thallium	*Biscutella laevigata*	13,768 (1)	4
	Iberis intermedia	4,055 (1)	10
Uranium	*Atriplex confertifolia*	100 (0.5)	10
Zinc	*Thlaspi calaminare*	10,000 (100)	4

d.w. = dry weight.

[a] Induced hyperaccumulation using ammonium thiocyanate.

NB: values in parentheses are mean concentrations usually found in non-accumulator plants.

kg of Ni/ha. There was no correlation between the age of a plant and its Ni content. The long-term cropping sustainability of the soils was simulated by sequential extractions with potassium hydrogen phthalate solutions at pH 2, 4 and 6 (Robinson et al., 1999) that showed a limiting plant-available Ni concentration of 768 mg/kg. Thus, seven croppings would reduce the plant-available Ni pool by 30%. A proposed model for phytomining (Robinson et al., 1997a) involved harvesting the crop after 12 months and burning the material to produce a sulphur-free bio-ore with about 11% Ni.

Fig. 2. *Alyssum bertolonii* — a nickel hyperaccumulator from Tuscany, Italy. The dried leaves contain on average about 1% (10,000 mg/kg) nickel.

2.3. Studies with Berkheya coddii

The third recorded phytomining field trials for Ni (Robinson et al., 1997b) used the South African Ni-hyperaccumulator *Berkheya coddii*. Field trials in New Zealand showed that a dry biomass of 22 t/ha could be achieved after moderate fertilisation (N + P + K). Pot trials showed enhanced biomass and relatively higher uptake of Ni with increasing nitrogen addition, but no increase with phosphorus. The Ni content of the plant was directly related to the ammonium-acetate-extractable fraction of Ni in a wide range of natural and artificial substrates. Excision of shoots induced a dramatic increase in the Ni content in the new growth (5500 mg/kg compared with 1800 mg/kg Ni). When plants were grown in pots with Ni added to the substrate (0–1%), Ni concentrations in the plants rose to a maximum value of about 10,000 mg/kg (1%) dry mass. The data from this last experiment were used to calculate the probable Ni yield (kg/ha) of plants grown in Ni-rich soils in different parts of the world, assuming non-limiting soil moisture. Moderately contaminated soils (100 mg/kg Ni) could be phytoremediated with only two crops of *Berkheya coddii*. The potential of this species for phytomining was also evaluated and it was proposed that a yield of 100 kg/ha of Ni should be achievable at many sites worldwide with applied fertiliser and adequate moisture.

3. Phytomining for thallium

3.1. Introduction

This subsection reviews phytomining for Tl and presents previously unpublished data on Tl in plants. We have recently discovered unusually high hyperaccumulation of Tl by the brassicaceous *Iberis intermedia* Guersent (candytuft) and *Biscutella laevigata* L. growing over lead/zinc mine tailings at Les Malines (Les Avinières) near Montpellier, France (Leblanc et al., 1999). Tailings typically contain 1.5% Zn and 0.5% Pb, and locally up to 40 mg/kg (mean 10 mg/kg) Tl. The mine dumps and substrate overburden are colonised by a typical base metal flora dominated by *Thlaspi caerulescens* (a hyperaccumulator of both Zn and Cd), *Biscutella laevigata*, *Iberis intermedia*, and *Minuartia verna* (a non-accumulator).

Thallium is extremely toxic and is used both in rat poison and for the control of ants. It also has uses in the electronics industry in semiconductors, switches and fuses. Thallium minerals are quite rare (0.7 mg/kg in the Earth's crust — Green, 1972), and are found almost exclusively in the realgar deposits of Allchar (Alsar) in Macedonia near the Greek border. They occur as complex sulphides of As–Hg–Tl (lorandite, picopaulite, raguinite, vrbaite) associated with realgar and iron sulphides. High concentrations of Tl have been reported in plants growing in the Allchar area (though not to the extent reported in this present paper) and have been found to cause toxic effects on local cattle (Zyka, 1970). The current world price of Tl is about $ US 300,000/t with production of only a few tonnes per annum.

Scientists at Hohenheim University, Stuttgart, Germany are investigating possible phytoremediation of soils polluted by heavy metals such as Cd, Zn and Tl (Kurz et al., 1997). Their work has shown that Tl is accumulated by food crops, particularly brassicaceous plants, and they have recommended that these should not be grown in such contaminated soils. Research in France on the same topic (Tremel, 1996; Tremel et al., 1997; Tremel and Mench, 1997) has found concentrations of up to 20 mg/kg (dry weight) Tl in vegetables (particularly in cabbage) and up to 40 mg/kg in rape (*Brassica napus* L.).

Thallium concentrations in plants have excited the most interest from scientists concerned with potential harmful effects on animals and humans. The potential of using hyperaccumulation in some plants in order to phytoremediate Tl-contaminated soils, or even to grow a 'crop of Tl' as has already been proposed for Ni (Robinson et al., 1997a,b), has been overlooked so far.

3.2. Thallium accumulation by selected plant species

Both *Biscutella laevigata* and *Iberis intermedia* from Les Malines in southern France contained very high levels of Tl of up to 1.4% dry weight in *Biscutella* and 0.4% in *Iberis* in the dry matter (Table 2). This present paper is the first record of the hyperaccumulator status of *Biscutella laevigata* in regards to Tl. The very high concentrations of Tl in these

Table 2
Thallium concentrations (mg/kg, dry weight) in plants and soils from France and Italy

Species	*N*	Location	A	B	C	B/C
Biscutella laevigata	3	Avinières, France (L)	244–308	291	28	10.4
	1	Aveyron, France (L)	43	43	–	–
	4	Avinières, France (S)	125–255	187	28	6.7
	1	Avinières, France (F)	428	428	28	15.3
	34	Avinières, France (W) [a]	20–15,199	480	28	17.1
	15	Tuscany, Italy (W)	<1–2	<1	<1	–
Iberis intermedia	19	Avinières (L)	47–3070	1190	16	74
	3	Avinières (S)	39–64	54	16	3.4
	3	Avinières (F)	313–522	422	16	27
	1	Avinières (R)	5.5	5.5	18	0.3
	26	Avinières (W) [b]	21–4055	372	16	23.2

N = number of specimens. A = absolute range of Tl in plants; B = geometric mean of Tl in plants; C = geometric mean of Tl in soils; B/C = plant soil Tl concentration quotient; F = flowers; L = leaves; R = roots; S = stems; W = whole plant.

[a] Standard deviation range was 124–1116 mg/kg.

[b] Standard deviation range was 48–4723 mg/kg.

plants cannot be derived from wind-borne contamination by soil, since the Tl concentrations in plant material are much higher than in the soil and the effect of soil-derived contamination would actually have been to lower plant Tl concentrations. The data in Table 2 were obtained from analyses performed by both flame and graphite-furnace atomic absorption spectrometry. Quality control was effected by replicate randomised analyses by inductively coupled plasma emission mass spectrometry that was initially responsible for identification of hyperaccumulation of Tl by our studied plants.

3.3. Phytomining for thallium

With a biomass of 10 t/ha as determined from field observations in France and field trials in New Zealand, the *Iberis* should produce about 700 kg/ha of bio-ore containing 8 kg of Tl, worth $ US 2400 at the current world price of $ US 300,000/t. There is clearly potential for phytomining for Tl if sufficiently large areas of contaminated soils are available in order to obtain the advantage of large-scale production. To be economic, phytomining should be able to produce $ US 500 per hectare irrespective of additional revenue from incineration of the biomass to generate electricity. For such a scenario, a crop with a biomass of 10 t/ha would have to contain at least 170 mg/kg Tl in dry matter, a level attainable with *Iberis intermedia* since 68% of our recorded values were above this threshold. *Biscutella laevigata*, at 4 t/ha has less than half of the biomass of *Iberis* but three times the mean Tl concentration. *Biscutella* would have to contain on average about 425 mg/kg Tl to achieve $ US 500/ha. About 39% of the plants analysed by us (Table 2) exceeded this concentration threshold.

The potential yield of saleable power by incineration of the biomass could add $ US 131/ha to the *Iberis* crop and $ US 53/ha to that of *Biscutella* using the assumptions of Nicks and Chambers (1998). However, sale of the energy would require a large-scale operation or alternative sources of biomass/rubbish to keep the generating plant operating for the whole year.

4. Phytomining for gold

The discussion so far has centred around the use of *natural hyperaccumulators* for phytomining. An alternative strategy uses *induced hyperaccumulation* whereby plants are induced to take up metals by solubilising them in the soil solution and allowing them to be taken up passively. This approach has been developed commercially (Blaylock et al., 1997) for phytoremediating soils contaminated with heavy metals such as lead. EDTA is applied to the soil to solubilise Pb. Numerous plant species can attain concentration levels as high as 1% in the dry tissue using this technique. An analogous approach used by Anderson et al. (1998) described induced hyperaccumulation of Au for phytomining.

The form of Au present in an area of mineralisation dictates the concentration of the metal introduced into soil solution after addition of thiocyanate as a chelating agent. Anderson et al. (1998) compared several auriferous substrates and their degree of extractable metal. The material with the greatest relative degree of extractable Au was acidic sulphide mine tailings. This material had the lowest total metal but contained heavily weathered residual Au. Reduced sulphide ore had the highest total Au content but very little extractable metal. Inducing Au-hyperaccumulation from this particular substrate has not been successful although the Au in this material could by solubilised by addition of thiosulphate.

An artificial, finely disseminated Au ore (5 mg/kg) was also prepared to reduce background variability in glasshouse experiments. *Brassica juncea* was chosen for a series of pot trials because of its high biomass and rapid growth rate. After approximately 3 weeks growth in pots of different auriferous substrates, the growth media were treated with 0 to 0.62 g/kg ammonium thiocyanate. The above-ground parts of each plant were harvested a week later, dried and ashed at 550°C. The ash was digested in aqua regia before analysis by graphite furnace atomic absorption spectroscopy. Hyperaccumulation of Au was achieved above a thiocyanate treatment level of 0.16 g/kg (Fig. 3) with a maximum individual value of 57 mg/kg Au. The values overall were very variable, probably because of the dichotomy of variable rate of plant death and the consequent variation of allowable time for Au uptake. A similar experiment grew *Brassica juncea* in a medium containing 5 mg/kg Au prepared from finely powdered native Au (44 μm) and treated with ammonium thiocyanate at an application rate of 0.25 g/kg (Fig. 3). The average Au in leaves compared well with that of the finely disseminated Au experiment.

Phytomining could be used to extract Au from tailings areas that contain concentrations of Au at a level uneconomic for conventional extraction techniques. In the initial stages of a revegetation programme, phytomining could also be used to extract Au from low-grade ore that many mining companies stockpile against expected increases in the gold price.

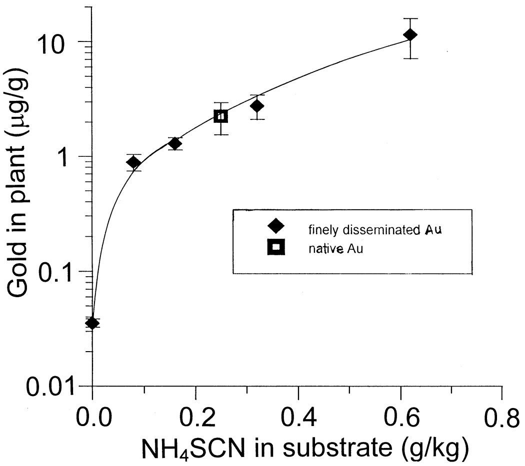

Fig. 3. Thiocyanate-induced uptake of gold by Indian mustard (*Brassica juncea*) from finely disseminated (solid diamonds) and native (open square) gold substrates containing 5 mg/kg (ppm) gold.

There are environmental concerns related to adding complexing agents or other chemicals to soils or tailings. The biodegradation pathways of ammonium thiocyanate to ammonia, bicarbonate and sulphate have been well studied (Hung and Pavlostathis, 1997). Despite a toxicity that is low relative to cyanide, use of thiocyanate would have to be strictly controlled to prevent leaching into ground and surface waters of this chemical and associated metals not taken up by plants. Leaching of the Au solution from the root zone is certainly not desirable in a phytomining operation. It might also be possible to use transgenic plants expressing a bacterial thiocyanate degrading system in order to extract Au from auriferous substrates (C. French — pers. commun., 1997). Such an approach would solve the problem of thiocyanate toxicity to plants and perhaps allow them to extract more Au, but not non-target metals.

5. Model of a phytomining operation and its economics

A model of a proposed economic scheme for phytomining is shown in Fig. 4. This system applies

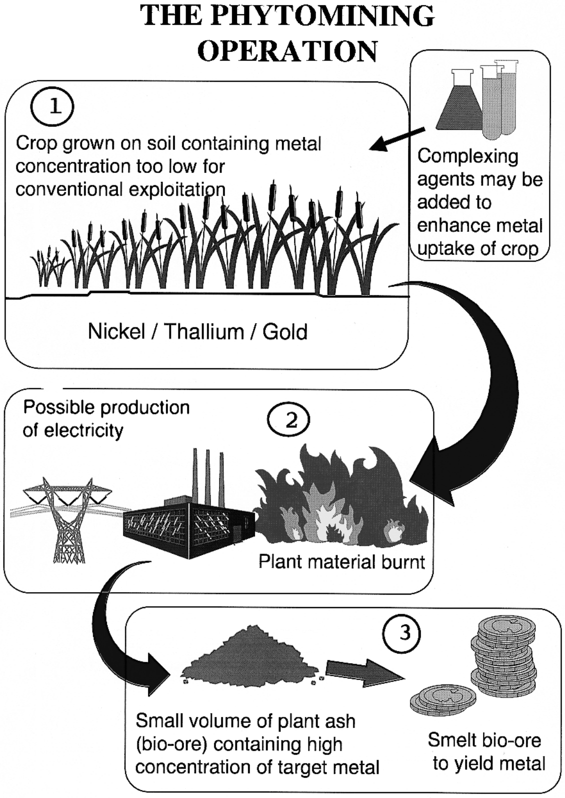

Fig. 4. Model of a proposed system for phytomining for metals.

to either natural or induced hyperaccumulation. In the latter case, the cost of the reagent has to be taken into account. The economics of the operation are dependent on a number of factors such as the metal content of the plant, its biomass production per annum, and whether or not the energy of combustion of the biomass can be recovered and sold.

Table 3 shows metal concentrations (mg/kg dry mass) required to provide a $ US 500/ha return for phytomining crops of different biomass, excluding the sale of energy from combustion of the plant material. When the pioneering field trials on phytomining were carried out in 1994 by Nicks and Chambers, the world price of Ni was $ US 7650/t (Nicks and Chambers, 1998). The halving of this price since that year can be expressed in terms of the economics of phytomining. In 1994 *Berkheya coddii* with a biomass of 20 t/ha needed only 3340 mg/kg Ni in dry mass (easily attainable) to recoup $ US 500/ha, neglecting the sale of energy of combustion. Today, phytomining is marginal for Ni despite a recent price upturn and it would require 6160 mg/kg for the same yield. The energy sale would be needed to make the project viable. It is clear that phytomining, like any other type of mining, will be dependent on world commodity prices.

It may well be argued that the economics of phytomining should not be compared with an agricul-

Table 3
Metal concentration (mg/kg dry mass) in vegetation of different biomass needed to provide a crop with a value of $ US 500/ha excluding sale of energy of biomass combustion

Metal	$ US/t	Biomasss yield (t/ha)				
		1	10	15	20	30
Platinum[a]	12,500,000	40	4.0	2.7	2.0	1.3
Gold[a]	10,714,000	47	4.7	3.2	2.3	1.5
Palladium[a]	3,787,000	130	13	8.8	6.6	4.3
Thallium	300,000	1,670	167	111	83	56
Silver[a]	152,113	3,280	328	218	164	109
Cobalt	48,000	10,400	1,040	694	521	347
Uranium	22,000	22,700	2,270	1,520	1,140	758
Tin[a]	5,580	88,700	8,870	5,910	4,400	3,000
Nickel	4,000	123,000	12,300	8,220	6,160	4,190
Cadmium	3,750	133,000	13,300	8,890	6,690	4,440
Copper	1,964	255,000	25,500	17,000	12,700	8,500
Manganese	1,700	294,000	29,400	19,600	14,700	9,800
Zinc	1,192	417,000	41,700	27,800	20,900	13,900
Lead[a]	577	869,000	86,900	57,900	43,500	30,000

[a] Induced hyperaccumulation probably required.

tural scenario because the former is concerned with a finite resource that can be depleted whereas the latter is not. However, Robinson et al. (1999) have shown that up to ten successive crops of Ni could be removed from nickeliferous soils before there was any noticeable reduction in the metal content of the substrate. Phytomining for Ni from the extensive lateritic soils of Cuba and New Caldeonia, for example, could exploit a virtually limitless resource.

Sale of energy in a phytomining operation is often a sine qua non for the project to be economic. It must be appreciated that this energy dividend also has to be set against agronomic costs such as site preparation, fertiliser application (if needed) and seed.

Phytomining technology has the following unique features:

(1) It offers the possibility of exploiting ores or mineralised soils that are uneconomic by conventional mining methods.

(2) ‘Bio-ores’ are virtually sulphur-free, and their smelting requires less energy than sulphidic ores.

(3) The metal content of a bio-ore is usually much greater than that of a conventional ore and therefore requires less storage space despite the lower density of a bio-ore.

(4) Phytomining is a ‘green’ technology that should appeal to the conservation movement as an alternative to opencast mining of low-grade ores.

Phytomining has, however, not yet been tested on a commercial scale and much research remains to be carried out, particular in the field of increasing metal uptake by plants either by genetic manipulation or addition of specific reagents to the soil, and the potential leaching of metals during induced hyperaccumulation. It is only then that we shall know the true value of this proposed technology.

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