Phytomining

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Phytomining is the production of a 'crop' of a metal by growing high-biomass plants that accumulate high metal concentrations. Some of these plants are natural hyperaccumulators, and in others the property can be induced. Pioneering experiments in this field might lead to a 'green' alternative to existing, environmentally destructive, opencast mining practices. Phytomining for a range of metals is a real possibility, with the additional potential of the exploitation of ore bodies that it is uneconomic to mine by conventional methods.

Plants able to accumulate high concentrations of heavy metals are known as hyperaccumulators[1]. The concentrations accumulated are 100 times those that occur in non-accumulator plants growing in the same substrates. For most elements the threshold concentration is 1000 $\mu g\ g^{-1}$ (0.1%) dry mass, except for zinc (10 000 $\mu g\ g^{-1}$), gold (1 $\mu g\ g^{-1}$) and cadmium (100 $\mu g\ g^{-1}$). About 300 species hyperaccumulate nickel, 26 cobalt, 24 copper, 19 selenium, 16 zinc, 11 manganese, one thallium and one cadmium[2] (Table 1). Most of these plants were regarded as scientific curiosities until it was proposed[3,4] that some might be used to produce a crop of a metal. Such a 'phytomining' operation would entail planting a hyperaccumulator crop over a low-grade ore body or mineralized soil, and then harvesting and incinerating the biomass to produce a commercial 'bio-ore'. Since the initial proposal of 1983 (Ref. 3), a US Patent has been taken out on phytomining for specific metals including nickel[5].

Pioneering phytomining trials

Following earlier proposals[3,4], intensive field trials were designed specifically to study phytomining *per se* rather than as an adjunct to phytoremediation. The trials were carried out at the US Bureau of Mines (Reno, Nevada)[6–8] on a naturally occurring stand of *Streptanthus polygaloides* (Fig. 1), which is a species known to hyperaccumulate nickel[9]. The soil at the site contained about 0.35% nickel, well below an economic concentration for conventional mining. It was proposed[6–8] that a net return of \$513 ha^{-1} to the grower could be achieved, assuming that:

- A minimum of selective breeding produced plants with 1% nickel in dry mass.
- The world price of nickel was \$7.65 kg^{-1}.
- The biomass yield after moderate fertilization was 10 t ha^{-1}.
- A quarter of the energy of combustion of the biomass could be turned into electricity for a yield of \$131 ha^{-1}.
- The return to the grower would be half of the gross yield of \$765 for the metal plus the energy yield of \$131.

This compares well with the average returns from other crops, and is well in excess of the average profit made by wheat farmers in the USA.

Table 1. Specific hyperaccumulators that might be used for phytomining[a]

Element	Species	Concentration	Biomass	Refs
Cadmium	*Thlaspi caerulescens*	3000 (1)	4	17
Cobalt	*Haumaniastrum robertii*	10 200 (1)	4	18
Copper	*Haumaniastrum katangense*	8356 (1)	5	18
Lead	*Thlaspi rotundifolium* subsp.	8200 (5)	4	19
Manganese	*Macadamia neurophylla*	55 000 (400)	30	20
Nickel	*Alyssum bertolonii*	13 400 (2)	9	21
	Berkheya coddii	17 000 (2)	18	22
Selenium	*Astragalus pattersoni*	6000 (1)	5	23
Thallium	*Iberis intermedia*	3070 (1)	8	24
Uranium	*Atriplex confertifolia*	100 (0.5)	10	23
Zinc	*Thlaspi calaminare*	10 000 (100)	4	25

[a]Concentrations are mean highest elemental values ($\mu g\ g^{-1}$ dry matter); values in parentheses are equivalents for non-accumulator plants. Biomass is t ha^{-1} yr^{-1}.

Fig. 1. A 'crop' of nickel in *Streptanthus polygaloides* growing on nickel-rich soils at Red Hills near Chinese Camp, California, USA.

The hyperaccumulator *Alyssum bertolonii*

As a sequel to the *S. polygaloides* project[6–8], experiments were carried out in Tuscany, Italy on the potential use of the hyperaccumulator *Alyssum bertolonii* in phytomining for nickel in nickel-rich ultramafic ('serpentinic') soils containing high concentrations of chromium, nickel and magnesium[10]. Fertilization (N + K + P) increased the biomass of reproductive matter threefold to 9.0 t ha^{-1} without dilution of the unfertilized nickel content of 0.8%. A nickel content of 0.8% in dry matter (11% in ash) gave a nickel yield of 72 kg ha^{-1}. Although the nickel content of 0.8% was below the ideal threshold of 1% proposed for the *S. polygaloides* study[6–8], a biomass yield of 12 t ha^{-1} can be achieved (as shown by field trials in New Zealand, with a second crop in the early autumn; R.R. Brooks *et al.*, unpublished data). Assuming a biomass yield of 12 t ha^{-1} containing 0.8% nickel, a nickel crop of 96 kg ha^{-1}, comparable with that achieved with *S. polygaloides*, should be expected.

The South African hyperaccumulator *Berkheya coddii*

Pot and field trials have been carried out with the nickel hyperaccumulator *Berkheya coddii*[11] to establish its potential for phytomining. Trial plots showed that a dry biomass of 22 t ha^{-1} could be achieved after moderate fertilization. Pot trials with varying soil amendments of nitrogen and phosphorus fertilizers showed enhanced uptake of nickel with increasing nitrogen addition, although there was no response to phosphorus.

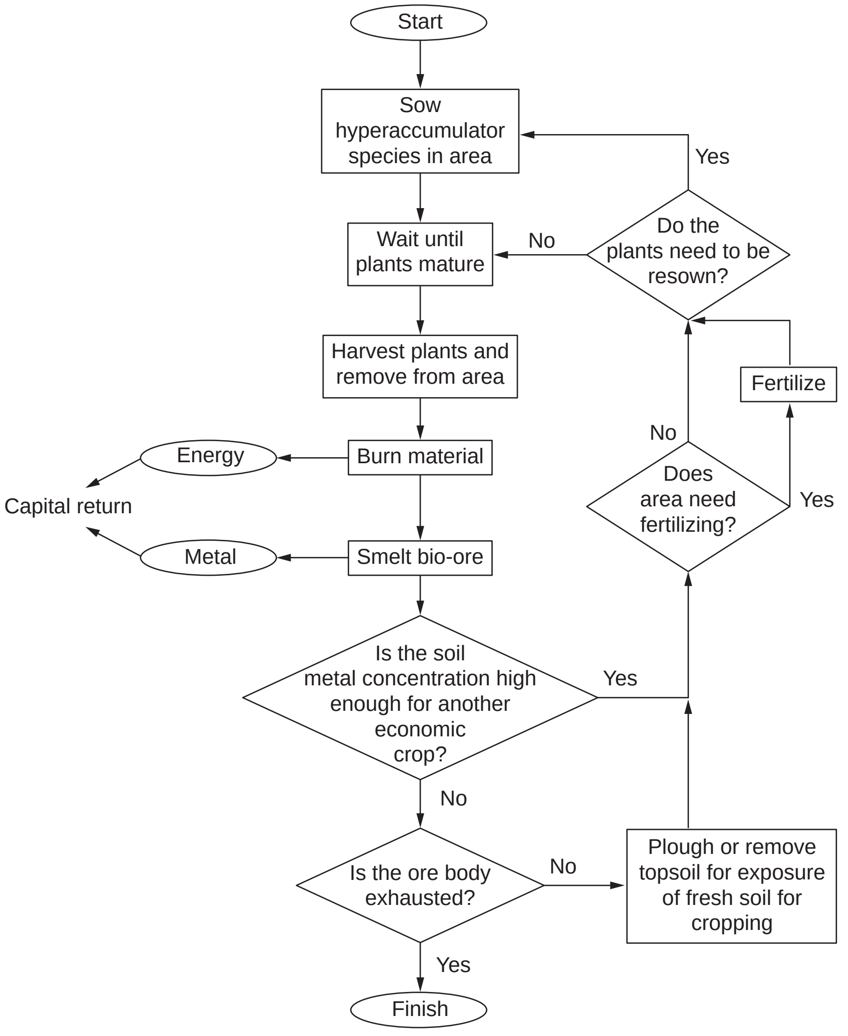

Fig. 2. Model of a possible economic phytomining system.

The nickel content of the plant was directly related to its extractable fraction in ammonium acetate in a wide range of natural and artificial substrates. Excision of shoots induced a dramatic increase in the nickel content in the new growth of the whole plant (5500 μg g^{-1} compared with 1800 μg g^{-1}). When plants were grown in pots with 0–1% nickel added to the substrate, the metal content of the plants rose to a maximum value of about 1% dry mass.

At the highest recorded concentration of 7880 μg g^{-1} nickel in whole wild plants in South Africa, a 1 ha crop of *B. coddii* would remove 168 kg of nickel, a yield equivalent to \$1285 assuming the value of nickel to be \$7.65 kg^{-1}. This, combined with the energy derived from the combustion of the plant material (\$288), translates to \$1311 ha^{-1}. If half of the value of the metal crop could be returned to the producer, this would represent about twice the value of a wheat crop.

Extreme caution must be applied in extrapolating the results of pot trials and limited field trials to large-scale metal farming. It has not been possible so far to achieve experimentally the 7880 μg g^{-1} nickel found in *B. coddii* wild plants; 5000 μg g^{-1} nickel seems a more realistic concentration and could provide a nickel yield of 110 kg ha^{-1}. Adding the energy profit and assuming a 50% return to the grower, the value of the crop is still well above that of a wheat crop, although worth only about the same as wheat if the energy bonus is discounted. The earlier work on phytomining was based on the then world price of \$7.65 kg^{-1} of nickel.

B. coddii has several advantages over other candidates for phytomining in the USA:

- Its biomass production is superior to that reported for any other hyperaccumulator except *Alyssum lesbiacum*[12] and is not at the expense of nickel content.
- The plant is easy to grow from seed.
- It is a perennial that can be harvested and regrown the following year without the need for resowing.
- Preliminary observations indicate that the nickel content of regrowth tissue is significantly higher than that of first-year growth.
- It is tolerant of cool climatic conditions including frost.
- Although probably tolerant only of mild winters, the plant could be grown as an annual crop in areas where winters are severe.
- It produces seed readily for future crops, and the flowers are easily fertilized by local bees; in South Africa they appear to be fertilized by a local species of flying beetle.
- It appears to be resistant to insect attack and soil pathogens.

Phytomining for metals other than nickel

There are practical limits to phytomining[13]. The main variables that control its economic feasibility are: the metal price, the plant biomass, and the highest achievable metal content of the plant (Table 2). Metal values range from about \$15 000 000 t^{-1} for platinum to about \$600 t^{-1} for lead. At these extremes, a plant with a biomass of 20 t ha^{-1}, such as *B. coddii*, would need to contain about 1.7 μg g^{-1} platinum or >4% lead. To achieve either target would require some type of substrate modification because natural concentrations of these two metals in dry plant material do not usually exceed 0.1 μg g^{-1} for platinum and 5 μg g^{-1} for lead. The lead content of maize with a biomass of 30 t ha^{-1} can be raised to close to the economic limit of 3.0% by adding EDTA to the substrate[14]; however, the cost of the EDTA alone would exceed the value of the lead extracted from the soil.

The work on lead highlights the two main approaches to phytomining[14]. The first of these is the less expensive and involves selection of plants of high biomass that are natural hyperaccumulators of the target metal. The use of *B. coddii* is a good example of this approach. Hyperaccumulator plants might realistically also be expected to be used for the elements thallium, cobalt, uranium and nickel (Tables 1 and 2), whose world prices lie in the range \$6000–300 000 t^{-1}. For the less valuable metals (tin to lead in Table 2) phytomining will never be a viable proposition.

The second approach to phytomining relies on the concept of induced hyperaccumulation, in which a chemical complexing agent must be added to the substrate (as described for lead)[14]. This is economic only for the most valuable metals, such as gold, silver and the platinum-group metals platinum and palladium, where the cost of the additive should be more than offset by the value of the product.

In a third scenario, the use of hyperaccumulator plants to decontaminate polluted soils[15] (phytoremediation) might result in production of a ‘bio-ore’ of some commercial value to recoup some of the costs of soil remediation.

Table 2. Metal concentrations (µg g^{-1} dry mass) in vegetation required to provide a total \$500 ha^{-1} return (excluding energy of incineration) on hyperaccumulator crops with varying biomass

		Biomass production (t ha^{-1})					
Metal	**(\$ t^{-1})**	**1**	**10**	**15**	**20**	**25**	**30**
Platinum[a]	14 720 752	34.0	3.4	2.3	1.7	1.4	1.1
Gold[a]	11 040 564	45.3	4.6	3.1	2.2	1.8	1.5
Palladium[a]	4 464 000	112.0	11.2	7.5	5.6	4.5	3.7
Thallium	300 000	1667	167	111	83	67	56
Silver[a]	152 113	3278	327	218	164	131	109
Cobalt	48 000	10 417	1042	694	521	417	347
Uranium	22 000	22 728	2273	1515	1137	910	758
Nickel	6090	82 164	8216	5477	4108	3286	2739
Tin[a]	5580	88 715	8871	5914	4435	3548	2957
Cadmium	3750	133 333	13 333	8889	6667	5333	4444
Copper	1964	254 970	25 497	16 998	12 749	10 199	8499
Manganese	1700	294 120	29 412	19 608	14 706	11 765	9804
Zinc	1192	417 076	41 707	27 805	20 853	16 683	13 902
Lead[a]	577	869 040	86 904	57 936	43 452	34 761	29 968

[a]Induced hyperaccumulation probably required.

Model of a possible economic phytomining system

A model economic phytomining system is shown in Fig. 2. The system differentiates between annual and perennial crops and takes into account fertilization and soil exhaustion. Whether a project succeeds will probably depend on whether some of the energy of combustion of raw material can be recovered. In tropical regions it should be possible to have crops maturing in each month, and thus keep the incineration plant busy throughout the year. It has also been suggested (R.L. Chaney, pers. commun.) that biomass could be stored in the field or near the incineration plant for burning according to the energy-requirement schedule.

Beyond the theoretical and pilot-plant stages of phytomining, two scenarios can be envisaged. The first is development of a large-scale commercial project involving square kilometres of metal-rich soils, such as those derived from ultramafic rocks or low-grade mineralization.

The second, and perhaps more likely, scenario is phytomining by smallholders throughout a region, in which a farmer might grow a few hectares of plant material and have it collected for processing at a nearby facility. This should be preferably close to a large city, where industrial waste could be used as feedstock for the incineration plant, which in turn could supply steam for producing local supplies of electricity. An obvious site for such small-scale phytomining is Brazil, where there are large areas of nickel mineralization and ultramafic soils from which it is uneconomic to extract metal conventionally. Farmers in Brazil are reported to have attempted and failed to grow crops such as soya bean over nickel-rich ultramafic soils[16]. The surrounding natural vegetation included several nickel hyperaccumulators that would have grown quite well as an alternative to failed soya bean crops.

Conclusions

Phytomining has several advantages over conventional mining. It offers the possibility of exploiting ore bodies or mineralized soils that are otherwise uneconomic to work, and its effect on the environment is minimal when compared with the erosion caused by opencast mining; the area to be mined may be ‘ready-vegetated’; a ‘bio-ore’ has a higher metal content than a conventional ore and therefore needs far less space for storage; and because of its low sulphur content, smelting of a ‘bio-ore’ does not contribute significantly to acid rain.

Extensive field trials are required to determine whether phytomining can become a reality. Its viability, like that of other mining methods, depends on the world price of the target metal. Such prices are subject to cyclical variation, and a low current value for a given metal should not preclude consideration of its extraction by phytomining. The biomass could be combusted immediately for its economic value and the plant ash stored until the world price improved.

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research focus

Chemical ecology in the molecular era

Chemical ecology is the study of chemical interactions between organisms and their environment. By analyzing the chemical traits that mediate interactions among organisms (such as the attraction of mates, dispersal of offspring, defense against enemies and competition for resources), researchers have implicated an ever-growing catalog of compounds. However, enormous challenges remain in elucidating the roles of individual chemicals and determining their evolutionary origins. For example, many plants produce complex mixtures of organic compounds that are thought to be important in defense against herbivores, but few experiments have demonstrated the function of the individual components. Genetic and molecular methods have great potential for addressing these questions.

Institute for chemical ecology

Research into the basis of the evolutionary forces that shape chemically mediated ecological interactions requires an interdisciplinary approach. This was the rationale for the new Max Planck Institute for Chemical Ecology in Jena, Germany. At a molecular level, researchers are seeking to characterize and elucidate the function of individual genes involved in the synthesis, storage, detection and metabolism of the compounds that mediate plant–pest interactions. Because plants play a central role in most ecosystems, and because they have developed a rich set of chemically mediated interactions with the community of heterotrophs that attack them, the chemical ecology of plants is the primary focus for research into the molecular and population genetics determining chemical traits. By bringing together researchers in ecology, population genetics, biochemistry, entomology, organic synthesis and analytical chemistry, the institute will be able to study the functional basis of chemically mediated ecological interactions in an interdisciplinary environment.

Evolutionary history

In 1888, Ernst Stahl, a professor in Jena, noted a pattern of reciprocal adaptation between plants and their insect herbivores[1]. The discipline of chemical ecology expanded throughout this century[2], and a landmark paper by Ehrlich and Raven[3] has shaped the research agenda in recent decades. They suggested a model of stepwise chemical coevolution between plants and insects, and proposed that antagonistic chemical interactions between plants and their natural enemies are primary factors responsible for the adaptive radiation of both plants and herbivorous insects. These historical interactions may be responsible for current patterns, where related plant species have similar secondary chemistry, and closely related insect taxa choose similar host plant species.

Subsequently, the concept of coevolution has been refined to distinguish between pairwise and diffuse coevolution[4]. Pairwise coevolution refers to a reciprocal, stepwise ‘arms race’ between an insect species and its host plant. Diffuse coevolution is more common, whereby several related insect species attack a range of plant species with similar chemical profiles. Although several herbivore and host species can have important impacts on each others’ evolution, tightly coevolving species pairs are probably rare[5].

In contrast to theories of chemical coevolution, the role that plant chemistry plays in determining insect host choice has recently been questioned[6] on the grounds that natural enemies of herbivorous insects might play a predominant part in determining insect host association. According to this view, plant secondary chemistry functions in other physiological roles, such as defense against UV-B radiation, drought, or other abiotic stresses. Alternatively, secondary metabolites might function in overflow storage or disposal of waste products from primary metabolism.

Molecular approaches

Questions about the adaptive origin and current function of plant secondary chemistry can be addressed using methods from molecular biology and evolutionary genetics, particularly via the isolation, characterization and manipulation of genes[7]. Here we illustrate several approaches that use physiological information, natural genetic variation, or molecular manipulations to understand the role and consequences of plant secondary chemistry.

Induction experiments

Inducible defenses may provide effective defense against attack by insect herbivores, while avoiding physiological costs of defense[8] when herbivory is absent. However, such presumed cost-savings and fitness benefits have not been demonstrated in nature. Ecological consequences of induced plant defenses can be studied using the wound-induced plant hormone jasmonic acid, which causes up-regulation of secondary chemicals in many plant species[9]. In the native, post-fire annual, *Nicotiana attenuata* (Fig. 1), the level of toxic nicotine increases after herbivore attack and is internally activated by jasmonic acid. In 745 matched pairs of *N. attenuata* plants growing in native populations, one member of each pair was treated with jasmonate methyl ester

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