Economic Geology
Vol. 94, 1999, pp. 109–114

The Phytomining and Environmental Significance of Hyperaccumulation of Thallium by *Iberis intermedia* from Southern France

MARC LEBLANC,
Géofluides-Bassins-Eau, CNRS, Université de Montpellier 2, Montpellier, 34095 France

DANIEL PETIT, ANNABELLE DERAM,
Laboratoire de Génétique et Evolution des Plantes, CNRS, Université de Lille 1, Villeneuve d'Ascq, 59655 France

BRETT H. ROBINSON, AND ROBERT R. BROOKS[†]
Soil and Earth Sciences, College of Sciences, Massey University, Palmerston North, New Zealand

Abstract

Unusual hyperaccumulation (>500 μg/g dry mass) of toxic Tl has been determined in *Iberis intermedia* (Brassicaceae) from southern France. This species contained up to 3,070 μg/g (0.31%) Tl in the whole-plant dry matter. Pot trials with *Iberis* showed that it could tolerate nearly 2,000 μg/g available Tl in the substrate compared with about 20 μg/g for the metal-tolerant grass *Arrhenatherum elatius*. This unusually high accumulation of Tl has significance for animal and human health, phytoremediation of contaminated soils, and phytomining for Tl. It was determined that three crops of *Iberis* would be sufficient to phytoremediate to a nontoxic level, a soil containing 10 μg/g Tl, and the production of a saleable plant ash (bio-ore) would probably pay for the cost of the operation. Phytomining (growing a "crop" of a metal over ores subeconomic for conventional mining) could be a viable option since it has been calculated that a net return of $1,200/ha (twice the return from a crop of wheat) would be possible with a biomass yield of 10 t/ha containing 0.08 percent Tl in dry matter. The break-even point (net yield of $500/ha) would require 170 μg/g (0.017%) Tl in dry matter. Such a project would, however, require a large area to be able to afford economies of scale.

Introduction

IN RECENT years there has been considerable interest in plants that hyperaccumulate heavy metals such as Cd, Co, Cu, Ni, Se, and Zn (Brooks, 1998). The concept of hyperaccumulation was originally introduced to define plants containing >1,000 μg/g (0.1%) of Ni in dried plant tissue (Brooks et al., 1977).

When hyperaccumulators of heavy metals were first discovered, their practical application was not fully appreciated until it was realized that they might be used in the fields of archaeology (Brooks and Johannes, 1990), mineral prospecting (Brooks, 1998), phytoremediation (McGrath et al., 1993), and phytomining (Chaney, 1983; Nicks and Chambers, 1995; Robinson et al., 1997a, b; Brooks et al., 1998). The last two subjects can be classified under the heading of "phytoextraction" and have excited perhaps the greatest amount of interest because of the use of plants to remediate polluted ground or even to grow a crop of a heavy metal such as Ni (Brooks, 1998) by planting a hyperaccumulator over subeconomic mineral deposits and harvesting the crop to produce a bio-ore.

We have recently discovered the unusually high hyperaccumulation of Tl by the brassicaceous *Iberis intermedia* Guersent (candytuft) growing over lead-zinc mine tailings at Les Malines (Les Avinières), some 40 km north of Montpellier, France. These tailings typically contain 1.5 percent Zn and 0.5 percent Pb, and locally contain up to 40 μg/g (mean 10 μg/g) Tl. The mine dumps are colonized by a typical base metal flora dominated by *Thlaspi caerulescens* (a hyperaccumulator of both Zn and Cd) and *Minuartia verna* (a nonaccumulator). *Iberis intermedia* is common throughout the area and clearly has a high tolerance of this type of substrate.

Thallium has an abundance of about 0.7 μg/g in the earth's crust (Green, 1972). It is frequently associated with sulfide mineralization and is commonly found to substitute for Pb in galena. Thallium is extremely toxic and has been used in rat poison and for the control of ants. It also has uses in the electronics industry for semiconductors, switches, and fuses. Thallium minerals are quite rare and are found almost exclusively in the realgar deposits of Allchar (Alsar) in Macedonia near the Greek border. They occur as complex sulfides of As-Hg-Tl (lorandite, picotpaulite, raguinite, vrbaite) associated with realgar and iron sulfides. High contents of Tl have been reported in plants growing in the Allchar area (although 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 $300/kg.

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 that these should not be grown in such contaminated soils.

Research in France on the same topic (Tremel, 1996; Tremel and Mench, 1997; Tremel et al., 1997) has found elevated concentrations of up to 20 μg/g (dry weight) Tl in vegetables (particularly in cabbage) and up to 40 μg/g in rape seed (*Brassica napus* L.).

Thallium concentrations in plants have excited the most interest from scientists concerned with potential harmful

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[†] Corresponding author: email, r.brooks@massey.ac.nz

0361-0128/99/2044/109-5$6.00

effects on animals and humans. Little or no attention has been paid to the potential of using hyperaccumulation in some plants in order to explore the possibility of phytoremediation of Tl-contaminated soils, or even to grow a "crop of Tl" as has already been proposed for other elements such as Ni (Robinson et al., 1997a, b). The present paper examines the potential of plants for this dual purpose with respect to Tl.

Geologic Setting

Samples were collected from sites around St. Laurent le Minier, southern France (Fig. 1). The site known as Les Avinières within the Les Malines mining region is part of one of the largest base metal mines in Europe that has been exploited since Roman times and ceased operations only in the early part of the present decade by which time it had produced about 1 Mt of metal (Zn + Pb).

The mine is located on the southern margin of the French Massif Central, along the contact between the Variscan basement (Cambrian shales and carbonates) and the Mesozoic cover (Triassic shales and carbonates, Liassic carbonates, Bathonian carbonates).

Intensive folding took place during the Hercynian orogeny, mainly in the late Carboniferous era. Extensive faulting occurred in the northern part of the area near St. Laurent le Minier, Montdardier, and Les Malines.

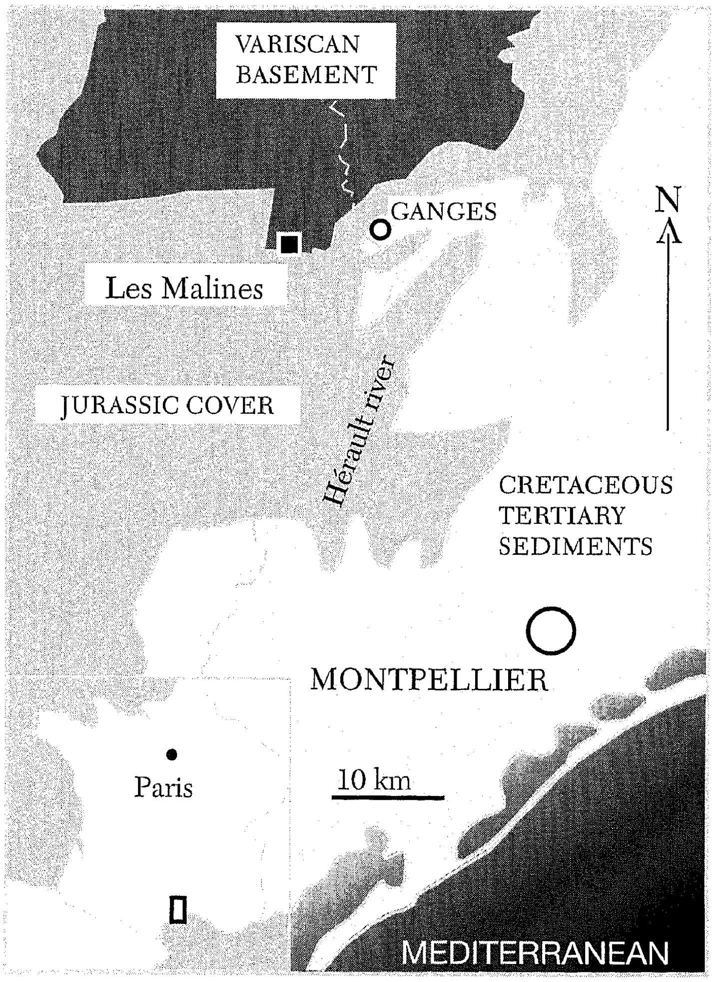

FIG. 1. Geologic map of the Les Malines (Les Avinières) base metal mining area near Ganges (Gard) some 40 km northwest of Montpellier, France.

The Les Malines mining district (Bosch et al., 1986) includes various orebodies belonging to different mineralization types (lenses within karst-filling sediments, stratiform lenses, veinlets, tectonic breccias, etc.) hosted in rocks of different ages (Cambrian, Triassic, Liassic, Bathonian) that are generally dolomitic rocks; these various orebodies may be ascribed to a type of Mississipi Valley mineralization. These different ore types result from a complex multistaged metallogenic evolution including remobilization processes. Consequently, the average metal contents vary strongly depending on ore type: i.e., from 3 to 50 percent Zn + Pb; the mean Zn + Pb quotient is about 4. Nevertheless, the mineral association is quite simple: pyrite, sphalerite, galena, barite, accessory Pb-Cu-(Ag) sulfosalts, and secondary oxidation minerals. Among the main trace metals (Cd, As, Sb, Tl, Ag) which are present within the Zn-Pb ores of Les Malines, thallium seems to be mainly associated with pyrite. The average Tl contents in ore material range from 3 to 35 μg/g depending on ore type.

Attempts are now being made to revegetate and ameliorate the enormous area of mine waste that now surrounds the little town of St. Laurent le Minier.

The pH of the tailings is typically 7.3 (mean of 60 samples), with a range of 6.4 to 7.7. The surprisingly high pH is due to the presence of calcareous material (e.g., $CaCO_3$) in the mine waste. This waste has been colonized by a typical metal-tolerant base metal flora dominated by *Minuartia verna* (L.) Hiern. and *Thlaspi caerulescens* with associated *Biscutella laevigata* L., *Iberis intermedia* Guersent, and *Armeria maritima* (Miller) Willd. Figure 2 is an illustration of *Iberis intermedia.*

FIG. 2. *Iberis intermedia* that can contain over 2,000 μg/g (0.2%) Tl in its dry tissues.

Methods and Materials

Sampling, preparation, and analysis of plant samples

For wild plants, Tl concentrations in dry whole plants or individual organs of *Iberis intermedia, Biscutella laevigata, Brassica napus, Silene cucubalus,* and *Thlaspi caerulescens* from Les Malines (Les Avinières) were collected, washed, and dried at 70°C. Plant samples (1 g) were digested with 10 ml of a 1:3 mixture of perchloric/nitric acids and heated in borosilicate beakers until fumes of perchloric acid were observed. The digests were then cooled and diluted to 10 to 20 ml, depending on the expected Tl content of the plant material.

A few samples were initially analyzed in France by plasma emission spectrometry (ICP-ES) in which dry material was originally ashed at 500°C for 3 h and the ash dissolved in dilute ultrapure sulfuric acid in order to provide solutions for analysis. Most of the samples were later analyzed in New Zealand by flame atomic absorption spectrometry (FAAS) using a GBC 904 instrument and the absorption line at 276.8 nm. In these later analyses, original samples were dissolved in mineral acids as reported above. Limits of detection for both ICP-ES and FAAS instruments were about 1 μg/ml for the solution presented for analysis, or about 5 μg/g for the original plant material. Agreement between the two methods was extremely close. The coefficients of variation in both cases for replicate analyses were <5 percent despite the different methods of sample attack. The data are shown in Table 1.

For pot trials, specimens of *Iberis intermedia* and the nonaccumulator grass *Arrhenatherum elatius* were grown in plant growth units in which we added Tl (as the acetate) to pots (500 ml) containing a standard commercial seed mix with added slow-release fertilizers. Thallium concentrations in these pots were nominally in the range of 0.1, 3, 6, 12, 24, 48, 98, 187, 375, 750, 1,500 and 3,000 μg/g dry weight.

Seedlings (five for each concentration of Tl) of *Iberis* and of the metal-tolerant grass *Arrhenatherum elatius* were introduced into each pot and grown for a period of three months in a temperature range of 15°C (night) to 25°C (day). The pots were placed over damp felt and watered weekly to prevent accumulation of salts at the surface. The period of three months brought the plants to a state of maturity just before the onset of flowering. Pots were moved at weekly intervals to standardize the amount of light received. Total aerial parts of all plants were washed in distilled water and digested with hot nitric acid (perchloric acid, initially used for field samples was later found to be unnecessary and was not used for the later pot samples). The resultant solutions were analyzed by FAAS as described above for wild plants.

Sampling, preparation, and analysis of soils and substrates

Field samples: The substrates in which the wild plants were growing consisted primarily of waste material from mining activities that had not been extant for a sufficient time to allow for the formation of discrete horizons and where the lack of organic material has prevented the formation of an upper humus layer. For each individual plant that was sampled, two "soil" samples were collected to a depth of 10 cm at opposite sides of the plant and made into a composite. Soil samples (ca. 250 g) were dried at 100°C and sieved to <2 mm size using a nylon sieve. About 10 g subsamples of sieved soil were ground using a mortar and pestle and then 0.2 g subsamples were accurately weighed into boiling tubes. Ten ml of concentrated nitric acid was then added to each tube and the mixtures boiled until a final volume of 3 ml was reached. A further 10 ml of concentrated hydrochloric acid was then added and the mixtures again evaporated to 3 ml. After filtration, the solutions were diluted to 100 ml with distilled water and then analyzed for Tl by FAAS as detailed above for plant samples.

Pot trials: After the harvesting stage, the Tl-rich substrates used for the pot trials were sampled by making a composite of three separate cores taken from each pot. The cores were taken with a 8-mm-diameter standard laboratory cork borer. The samples were dried and ground in a mortar and pestle followed by adding 5-g samples of sieved material into 150-ml polythene containers. Then 50 ml of 1*M* ammonium acetate was added to each container. Samples were gently agitated (75 rpm) for 24 h, filtered (Whatman No. 41), and stored in polythene containers. Ammonium acetate was chosen for the

TABLE 1. Thallium Concentrations (μg/g dry weight) in Plants and Soils from France (except where otherwise stated)

Species	*n*	Location[1]	A	B	C	B/C
Biscutella laevigata	3	Les Avinières (L)	244–308	291	28	10.4
	1	Aveyron (L)	43	43		
	2	Gailitz, Austria (L)	295–495	395		
	4	Les Avinières (S)	125–255	187	28	6.7
	1	Les Avinières (F)	428	428	28	15.3
Brassica napus	1	Carnoulès (W)	1,197	1,197	5	239
Iberis intermedia	19	Les Avinières (L)	47–3,070	1,190	16	74
	3	Les Avinières (S)	39–64	54	16	3.4
	3	Les Avinières (F)	313–522	425	16	27
	3	Les Avinières (L)	880–2,810	1,647	14	118
	3	Les Avinières (W)[2]		795	14	57
	1	Les Avinières (R)	5.5	5.5	18	0.3
Silene cucubalus	1	Les Avinières (W)	34	34	28	1.2
Thlaspi caerulescens	8	Les Avinières (W)	1–12	7	28	0.2

n = number, A = range in plants, B = mean in plants, C = concentration in soils to a depth of 10 cm, B/C = plant/soil concentration quotient

[1] F = flowers, L = leaves, R = roots, S = stems, W = whole plant

[2] Calculated from stem/leaf ratio of 55:45

experiments because of its well proven use as a measure of the plant-available fraction of soils (Ernst, 1996); this amounted to about 80 percent of the original total Tl content.

The pH measurements were made by shaking 4-g samples of soils or mine waste with 10 ml of distilled water for a period of 1 h. After being allowed to settle for 24 h, the samples were again shaken for a few minutes and the pH measured after an appropriate settling period.

Results and Discussion

Thallium in plants from Les Avinières

The data in Table 1 show that *Iberis intermedia* is able to hyperaccumulate up to 2,810 μg/g Tl in its dry leaves. This Tl is clearly not derived from windborne contamination by soil, since the Tl concentrations in plant material are much higher than those in the soil. The effect of soil-derived contamination would actually have been to lower rather than increase the apparent Tl content of the plants.

The initial investigation of wild plants indicated that *Biscutella laevigata* contained a maximum of 495 μg/g Tl, in itself an extraordinarily high level. But because this species has a lower Tl concentration and smaller biomass than *Iberis* (about half that of *Iberis*), it would not appear to be as useful as *Iberis* for phytoremediation or phytomining of Tl and was not investigated further.

Figure 3 is a plot of Tl concentrations in plant material (μg/g dry weight) shown as a function of the extractable Tl in the substrate. A similar type of plot (not shown) was obtained when the x axis consisted of the nominal total, rather than extractable, Tl. Figure 4 shows the biological absorption coefficient (plant/soil elemental concentration quotient) for Tl in the plants studied.

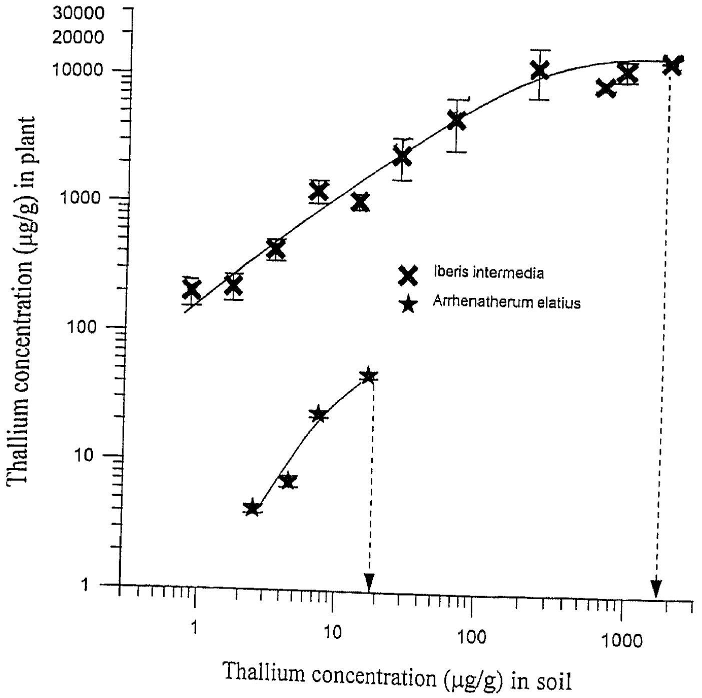

FIG. 3. Thallium concentrations in whole plants grown in artificial soils with different Tl concentrations (extractable fractions). Perpendicular lines show the limits of tolerance.

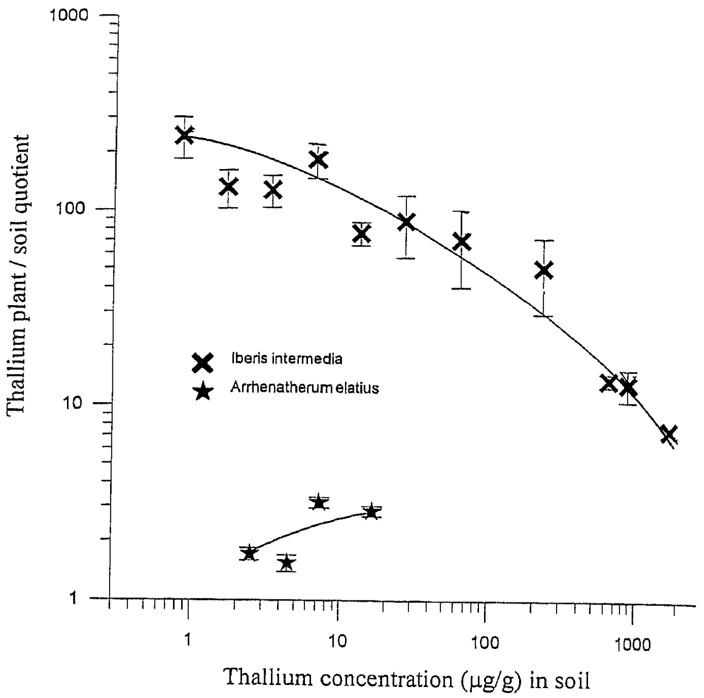

FIG. 4. The biological absorption coefficients (whole plant/soil elemental concentration quotients) as a function of extractable Tl in the substrate.

A number of conclusions can be deduced from Table 1 and Figures 3 and 4:

1. Leaves of wild specimens of *Iberis* show hyperaccumulation of Tl (here defined as >500 μg/g [>0.05%] in dry plant material).
2. Under greenhouse conditions, the biological absorption coefficients, among the highest ever recorded for hyperaccumulator plants, decrease with increasing amounts of Tl in the substrate and at low Tl levels (<10 μg/g) are on the order of 300, decreasing to about 10 over 500 μg/g Tl in the substrate Tl.
3. The nonaccumulator *Arrhenatherum* contained slightly more Tl than the substrate.
4. Based on Tl concentrations in experimental pots, the tolerance limit is about 1,800 μg/g Tl for *Iberis* and only 20 μg/g for the grass.
5. Mean Tl levels in both species increase in the sequence stems < leaves < flowers (Table 1).

It will be noted from Table 1 that high Tl levels were also found in a single specimen of *Brassica napus*. This is not unexpected because of the known propensity of brassicaceous plants to accumulate Tl, but we have not investigated this matter further.

Animal and human health significance of thallium in plants

The extraordinarily levels of Tl recorded in *Iberis intermedia* have important ramifications for human and animal health. It must be remembered that *Iberis intermedia* is a common weed in rocky or disturbed sites throughout central and southern Europe. These high levels of Tl found in *Iberis* pose a potential problem for animal husbandry, given the extremely toxic nature of this element (18.5 mg Tl/kg of body weight compared with 2.2 mg/kg for sodium cyanide; source: Stecher, 1968). Even when the Tl concentration in the soil is at crustal background levels (ca. 1 μg/g), the plants can contain over 100 μg/g Tl in dry tissue. High concentrations of Tl in brassicaceous food crops such as rape seed also present a potential problem for human health considerations when crop plants are grown over Tl-rich substrates as occurs frequently in France (Tremel et al., 1997) and Germany (Kurz et al., 1997).

Phytoremediation of thallium by use of plants

The high concentrations of Tl in *Iberis* afford the possibility of using this plant for phytoremediation of Tl-contaminated soils such as those which have been found near a cement works in southern Germany (Kurz et al., 1997) and along the borders of the Massif Central in France where the Triassic terrane is rich in Pb, Zn, and Tl (Tremel, 1996). A typical plant of *Iberis* weighs 30 g dry weight. Our own field trials have shown that 50 plants can be grown in 1 m^2 of soil. We can therefore envisage a biomass production of 15 t/ha. If we adopt a more conservative approach and give an estimate of 10 t/ha, whole plants containing on average 800 μg/g Tl would provide about 8 kg of Tl worth $2,400/ha at today's prices. Assuming that a contaminated soil containing 10 μg/g Tl is to be remediated to a depth of 20 cm and assuming a soil density of 1.3, a hectare of soil would weigh 2,600 t and would contain 26 kg of Tl. Assuming that the plant-available fraction of Tl remains constant at each growing season, three sequential crops of *Iberis intermedia* should in theory be sufficient to remove most of the Tl from this soil. If it were possible to sell the ashed biomass (bio-ore) for $7,200 over the three-year period, this would pay for the costs of remediation.

Phytomining for thallium

The concept of phytomining (Chaney, 1983; Nicks and Chambers, 1995; Robinson et al., 1997a,b; Brooks, 1998) involves growing a crop of a hyperaccumulator plant for the express purpose of producing a saleable ash (bio-ore). With a biomass of 10 t/ha and assuming an ash weight of 7 percent as determined by us experimentally, the ashed *Iberis* should produce about 700 kg of bio-ore containing 8 kg of Tl, worth $2,400 at the price of $300/kg. If only half of this sum were returned to the grower (i.e., after processing and costs of production), the resulting $1,200/ha is over twice the return of a crop of wheat to an American farmer (Nicks and Chambers, 1995). There is clearly some potential for phytomining for Tl but only if sufficiently large areas of contaminated soils are available in order to obtain the advantage of large-scale production. In order to be economic, phytomining should be able to produce $500 per hectare irrespective of any 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 μg/g Tl in dry plant matter, a level easily attainable with *Iberis intermedia*.

Conclusions

Hyperaccumulation of Tl by *Iberis intermedia* is the first case to be recorded in vegetation and should open up a number of fields of research involving not only phytoextraction of heavy metals but also the possibility of phytochemical studies to elucidate the mechanisms of this very unusual hyperaccumulation of a highly toxic heavy metal.

Most noteworthy is the possibility of using these plants for phytomining of Tl. Unlike metals such as Ni that have been shown to have a phytomining potential only if the world price of the metal remains high, Tl does not suffer the wild swings of price change experienced by many other metals and is at present perhaps the strongest candidate for successful phytomining in the future.

May 8, October 8, 1998

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