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The Phytoremediation Potential of Thallium-Contaminated Soils Using *Iberis* and *Biscutella* Species

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ABSTRACT

Biscutella laevigata and *Iberis intermedia* were sampled from sites near St Laurent le Minier, Southern France, and *B. laevigata* was also sampled from Rocca San Silvestro, Tuscany, Italy. Soils associated with the rhizosphere of each plant were also sampled. Both *Biscutella laevigata* and *Iberis intermedia* accumulate inordinately high concentrations of thallium (1.94 and 0.4%, respectively) in their above-ground dry tissue. The levels of thallium accumulated by both species were strongly correlated with both the total and extractable concentrations of thallium in the soils. Concentrations of zinc, cadmium, and lead were below the threshold for hyperaccumulation. It is proposed that *B. laevigata* and/or *I. intermedia* could be used for phytoremediation or phytomining of thallium-contaminated soils. Such an operation would involve the repeated cropping of either species, until an acceptable level of thallium in the soils was reached. Additionally, the harvested plant material could be burnt and the resulting ash smelted to produce an economically viable 'crop' of thallium.

KEY WORDS: thallium, phytoremediation, phytomining, *Iberis intermedia*, *Biscutella laevigata*.

I. INTRODUCTION

In recent years there has been growing interest in remediation technologies for the ever-growing problem of heavy metal-contaminated soils. Phytoremediation (Chaney, 1983; Brooks, 1998) has emerged as a potentially effective method for the *in situ* decontamination of soils weakly polluted with some heavy metals.

In a phytoremediation operation, a crop of plants is grown over a metal-polluted soil with the aim of removing the toxic elements. The plants used for phytoremediation accumulate (either naturally or by addition of a chemical to the soil) the target metal in their stems and leaves. The plants can then be harvested and burnt to reduce the volume. The resulting ash may be stored in a 'safe area', or, if the metal is of sufficient value, be smelted and sold to recoup some, or all, of the cost of the operation. When monetary return is the sole purpose of the operation, the technique is known as *phytomining* (Chaney, 1983; Brooks *et al.*, 1998). Plants used in a phytoremediation operation need to accumulate large quantities of the target metal in the aerial portions. Species that naturally accumulate heavy metals in their aerial portions are known as *hyperaccumulators* (Brooks *et al.*, 1977). These plants also tolerate very high elemental concentrations in the substrate and perhaps the hyperaccumulation trait is the reason why these plants are able to grow on metal-enriched soils. Other species can be induced to accumulate metals by the addition of chemicals to the soil. Ideally, the plants used in a phytoremediation operation should have a high biomass production, a high metal content, and be easily propagated.

Thallium is a group IIIA heavy metal that is even more toxic than mercury. Zitko (1975) reported an LD_{50} of 0.03 mg/L for Atlantic salmon. Thallium is toxic to plants by inhibiting seed germination and chlorophyll formation in many plant species (Zitko, 1975). Thallium pollution can derive from anthropogenic or pedogeochemical sources. Thallium has limited uses in industrial applications that include semiconductors and rat poisons. There is only one thallium-mining operation in the world, at Alsar in Macedonia. Many industrial operations produce thallium as a byproduct. Geochemically, thallium can substitute for lead in galena, which is another source of natural contamination.

The first studies on thallium uptake by plants were performed by Zyka (1970), who found up to 1.7% (dry mass) in *Galium* sp. growing near the Alsar mine. In a preliminary survey of thallium concentrations in plants growing over thallium-rich mine tailings at Les Aviniärés from southern France, recently, we have reported up to 2810 mg/kg (0.28%) thallium in dry leaves of *Iberis intermedia* (Leblanc *et al.*, 1999). This species is now classified as a hyperaccumulator of thallium. Lower concentrations of thallium were also reported in B*iscutella laevigata* by these same authors, although not at the level of hyperaccumulation. Both species are found growing wild in many locations throughout Europe and are not inhibited by high levels of thallium and pose a potential hazard to grazing animals.

Biomass experiments by Leblanc *et al.* (1999) indicated up to 15 t/ha of *Iberis intermedia* could be harvested. This degree of accumulation could pay for remediation costs if an economic method of recovery were to be employed. This also has ramifications for the related field of phytomining (growing an economic crop of a metal) because of the high value of thallium ($US300,000/t. Estimations of the feasibility of thallium phytomining have been given by (Anderson *et al.*, 1999).

French agrosystems typically have higher concentrations of thallium than those found in other countries. Tremel (1996) found a mean value of 1.513 mg/kg thallium in French soils, compared with Austria (0.30 mg/kg) and China (0.58 mg/kg). These high levels of thallium have prompted our own studies on phytoremediation/ phytomining by use of native French species.

The most extensive studies on the feasibility of phytoremediation for thallium have been centered at the University of Hohenheim, near Stuttgart, Germany (Kurz *et al.*, 1999). They have proposed using brassicaceous plants such as rape (*Brassica napus*) or green cabbage to phytoremediate soils for thallium. Kurz *et al.* (1997) showed that simultaneous croppings of rape and cabbage in the same growing season were able to remove 6 to 8% of the thallium burden in the top 30 cm of soil.

Although there has been some highlighting of the thallium problem in recent papers from France and Germany, it is still not recognized in the world community that this problem is much more widespread than previously recognised. This is because few previous studies had bothered to look at thallium among the plethora of other heavy metals such as cadmium, lead, and arsenic that had been the focus of so many previous studies. A thorough survey of sites polluted with coal ash or emission from base-metal smelters will surely pinpoint many other areas of concern in public and animal health. There is a further reason why phytoremediation of thallium should be investigated further. Thallium concentrations in polluted soils tend to be of the order or 1 to 2 mg/kg rather than the 1 to 2% found in soils polluted by lead/zinc base-metal emissions from smelters (e.g., at Auby in northern France). Levels as high as the latter will never be able to be phytoremediated, even by hyperaccumulators, in the foreseeable future, whereas, as shown by Kurz *et al.* (1997), thallium concentrations of the order of 1 mg/kg could be remediated in 5 to 10 years by use of rape or *Iberis intermedia.*

Recently, we have discovered thallium concentrations in *Biscutella laevigata* that are even higher than those previously reported for *Iberis intermedia*. The aims of the present study were therefore to: (1) extend the investigation of the uptake of thallium and other heavy metals in *Iberis intermedia* and *Biscutella laevigata* growing on soils with varying heavy metal contamination in France and Italy; (2) determine the relationship between the soil thallium concentrations (both total and extractable) and plant uptake; (3) investigate the solubility of thallium in these soils in relation to its total concentration; (4) investigate the potential of *I. intermedia* and *B. laevigata* for thallium phytoremediation and phytomining.

II. MATERIALS AND METHODS

A. Site Descriptions

Iberis intermedia and *Biscutella laevigata* were collected from sites around St Laurent le Minier, southern France, and Rocca San Silvestro, Tuscany, Italy (Figure1). The region around St Laurent le Minier, known as Les Malines, is the location of one of the largest base metal mines in Europe that has been exploited since Roman times and only ceased operations about 5 years ago. The mineralization consists of zinc/lead sulfides and oxides associated with barite. The mine tips typically contain several percent of both lead and zinc with associated thallium and cadmium. The pH of the tailings is 7.3 (average of 60 samples) with a range of 6.4 to 7.7. The mine

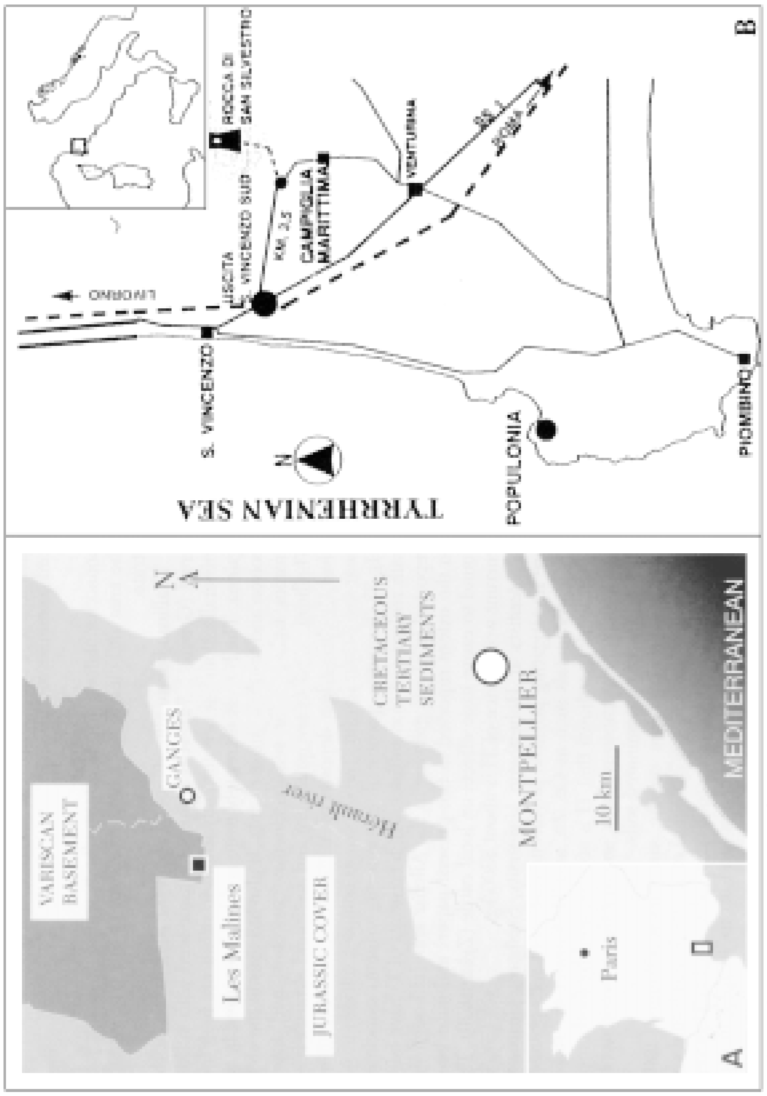

FIGURE 1. Location maps of collection sites for *Iberis intermedia* and *Biscutella laevigata* in (a) France and (b) Italy.

waste has been colonized by a base metal flora dominated by *Minuartia verna* (L.) Hiern. and *Thlaspi caerulescens* J. C. and R. Presl with associated *Iberis intermedia* Guersent, *Biscutella laevigata* L., and *Armeria maritima* (Miller) Willd.

The site near Rocca San Silvestro, Tuscany, Italy, was an ancient mining town where lead, copper, and silver have been mined since the tenth century. Geologically, the area consists of a limestone Massif with parallel veins of porphyritic rocks containing mixtures of sulfides (galena argentite, chalcopyrite, and blende) running in a southeast to northwest direction. The average pH of the soils is 7.3 (15 samples) with a range of 7.1 to 7.5.

B. Sample Collection

Iberis intermedia (15 plants) and *Biscutella laevigata* (37 plants) were sampled at various sites within Les Malines. *Biscutella laevigata* (15 plants) was also sampled from around Rocca San Silvestro. The rhizosphere soil was also sampled in addition to the above-ground biomass.

C. Plant Digestion

Plants were rinsed thoroughly in distilled water and dried at 80°C. Approximately 0.2 g of material from each plant was accurately weighed into 50-mL Erlenmeyer flasks. Concentrated nitric acid (10 mL) was added to each tube and the mixtures heated on a heating block until a final volume of ca. 3 mL was reached. The samples were then diluted to 10 mL using distilled water and stored in polythene containers.

D. Soil Digestion

Soil samples were dried at 80∞C and sieved to <1 mm size using a nylon sieve. About 0.2 g quantities of sieved soil were accurately weighed into boiling tubes. Ten mL of concentrated nitric acid was then added 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 dilution to a final volume of 10 mL with distilled water, the solutions were filtered.

E. Estimation of the pH and Plant-Available Elemental Fractions in the Soils and Mine Waste

Sieved soil (2 g) was weighed accurately into 50-mL centrifuge tubes. Then 20 mL of 1 *M* ammonium acetate was added to each container. Samples were shaken in an end-over-end mixer (75 rpm) for 24 h, filtered, and stored in polythene containers. Ammonium acetate was chosen for the experiments because of its common use as an approximate measure of the plant-available fraction of soils (Ernst, 1996).

The pH measurements were made by weighing 1-g samples of soils or mine waste into polythene containers, then adding 2.5 mL of distilled water and shaking. After being allowed to settle for 24 h, the samples were again shaken and the pH measured.

F. Chemical Analysis

Thallium, cadmium, copper, lead and zinc were quantified in the plant and soil solutions using a GBC 904 atomic absorption spectrometer.

III. RESULTS AND DISCUSSION

A. Accumulation of Metals by *Iberis intermedia* and *Biscutella laevigata*

The metal contents of plants and associated soils from St Laurent le Minier and Rocca San Silvestro are shown in Table 1. Because the data were lognormally distributed, geometric means are reported with the corresponding standard deviation ranges. Except for copper, values of all the metals measured are high relative to plants growing over nonmetalliferous soils. However, values for lead, cadmium, and zinc are well below the 'threshold' for hyperaccumulation (1000, 100, and 10,000 mg/kg, respectively; Brooks, 1998). The concentration of thallium in most plants was above the threshold of 500 mg/kg dry matter set by Leblanc *et al.* (1999) for *Iberis intermedia* from St Laurent le Minier. *Biscutella* specimens from Rocca San Silvestro were below this limit but were well in excess of it (up to 1.96%) at the French location. The lower values could be attributed to the lower soil thallium concentrations at the Italian site. The high levels of lead in most of the plants probably indicate some degree of soil contamination. However, because the thallium concentration in the plants was actually higher than the corresponding soil values, soil contamination will lower rather than raise the measured thallium concentration in the plant material.

B. Relationships between Plant-Metal Concentrations and Soil Properties for *Biscutella laevigata*

Table 2 shows a matrix of correlations for elemental concentrations in soils and specimens of *Biscutella laevigata* growing around St Laurent le Minier, southern France. Analogous data have already been presented for *Iberis intermedia* by Leblanc *et al.* (1999). The total elemental concentrations in the soils were all correlated with each other and with their respective extractable fractions. This is expected as all four elements are geochemically related and indicate the degree of metal-bearing mineral contamination in the soil.

Thallium concentrations in plants were correlated significantly with pH and with the total thallium concentration in the soil. The correlation between plant thallium and the extractable soil fraction of this element was much stronger than its correlation with the total thallium in soils. This reinforces the theory that it is the extractable, rather than the total fraction of a metal that determines plant uptake. Figure 2 shows the relationship between the thallium concentration in *B. laevigata* (from both French and Italian sites) and the extractable thallium concentration in the soil. There was no significant relationship between the levels of lead in the plants (indicating soil contamination because lead is not usually accumulated in plants via root systems) and the plant thallium concentration. This is further evidence that the high measured thallium values are not the result of wind-borne contamination.

Surprisingly, there was a significant positive correlation between plant thallium uptake and soil pH. Previous studies (e.g., Robinson *et al.*, 1998) have shown that the uptake of other heavy metals was negatively correlated with pH presumably due to the greater solubility of these metals under more acidic conditions.

TABLE 1. Mean (Geometric) Elemental Concentrations (mg/kg Dry Mass) in *Iberis Intermedia* and *Biscutella Laevigata* from St. Laurent le Minier (France) and Rocca San Silvestro (Italy)

	Thallium	Lead	Cadmium	Copper	Zinc
France					
I. intermedia	411 (141–1200)	111 (45–278)	9 (3–33)	8 (5–12)	630 (232–1710)
Soil	14 (5–43)	6106 (1860–20100)	122 (46–311)	55 (25–126)	25500 (9810–66100)
B. laevigata	504 (65–3920)	191 (76–470)	27 (6–121)	7 (4–13)	2290 (805–6530)
Soil	25 (11–57)	14600 (3960–54000)	273 (71–1050)	430 (29–6210)	56900 (17300–188000)
Italy					
B. laevigata	4 92–6)	45 (15–130)	4 (1–17)	133 (15–130)	432 (266–699)
Soil	1 (<1–3)	3791 (2732–5259)	46 (36–60)	683 (34–13808)	19730 (14337–27151)
Normal plants[a]					

Note: NB, Values in parentheses are standard deviation ranges because data were lognormally distributed.

[a] Mean elemental concentrations expected to be found in plants not growing over mineralization.

TABLE 2. Correlation Matrix for Heavy Metals in Plants and Associated Soils for *Biscutella laevigata* from Metal-Contaminated Soils at St. Laurent le Minier, Southern France

	pTl	**pZn**	**pPb**	**pCd**	**pH**	**sTl**	**sZn**	**sPb**	**sCd**	**eTl**	**eZn**	**ePb**
pZn	NS											
pPb	NS	S**										
pCd	NS	S**	S**									
pH	S	NS	NS	NS								
sTl	S*	S*	S*	NS	NS							
sZn	NS	S*	S**	S*	NS	S**						
sPb	NS	S*	S**	S**	NS	S**	S**					
sCd	NS	S*	S**	S*	NS	S**	S**	S**				
eTl	S**	PS	NS	NS	NS	S**	S	NS	NS			
eZn	S*	S*	S*	S*	NS	S**	S**	S**	S**	S*		
ePb	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	S*	
eCd	NS	NS	S*	NS	NS	S*	S**	S*	S**	NS	S*	NS

Note: p, concentration in plant; s, total concentration in soil; e, extractable concentration in soil. S**, very highly significant ($P < 0.001$); S*, highly significant ($0.001 \Leftrightarrow P < 0.01$); S, significant ($0.01 \Leftrightarrow P < 0.05$); PS, possibly significant ($0.05 \Leftrightarrow P < 0.10$); NS, not significant ($P \Leftrightarrow 0.10$).

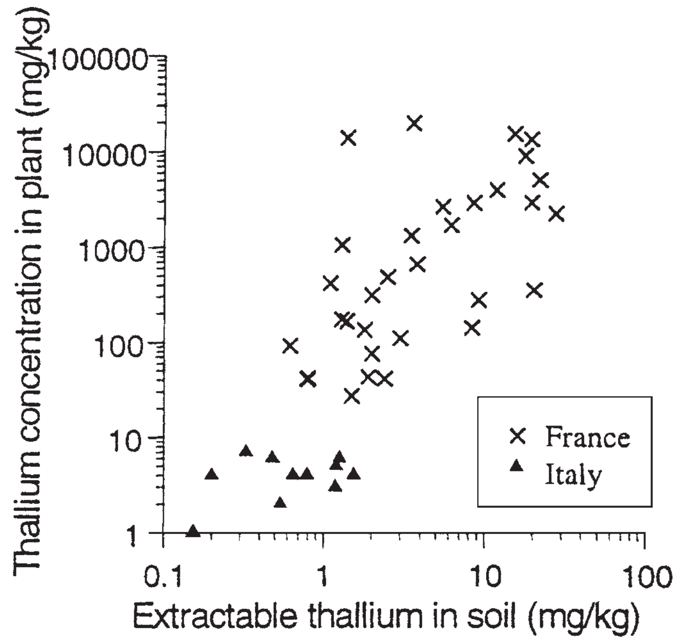

FIGURE 2. Uptake of thallium by *Biscutella laevigata* as a function of the extractable (1 *M* ammonium acetate) total thallium concentration in the soil.

C. The Relationship between Extractable and Total Thallium Concentrations in Soils

Figure 3 shows the percentage of the total metal concentration that is extractable using 1 *M* ammonium acetate. As a percentage of its total concentration, thallium was significantly ($P < 0.005$) more soluble than all the other metals tested and had the lowest total concentrations in soils. This is in contrast to numerous studies (e.g., Waitz and Percival, 1993) that have shown that in soils the percentage of a metal that is soluble increases as its total concentration increases. This relatively high solubility of thallium indicates that it could have a greater impact on biota than the other metals tested at low total concentrations.

To measure the extractable, rather than total, elemental concentrations in soils is not a new concept, but usually gives a much better estimate of the metal fraction "seen" by the plant than does the total concentration in the soil (Robinson *et al.*, 1997). A simple extraction with ammonium acetate of a soil intended for phytoremediation can give valuable preliminary information on the feasibility of carrying out phytoremediation in that particular instance.

D. The Potential use of *B. laevigata* and *I. intermedia* for Phytoremediation/ Phytomining of Thallium-Rich Soils

The greater solubility of thallium in soils means that more is available for plant uptake in phytoremediation/phytomining operations. The high bioaccumulation co-

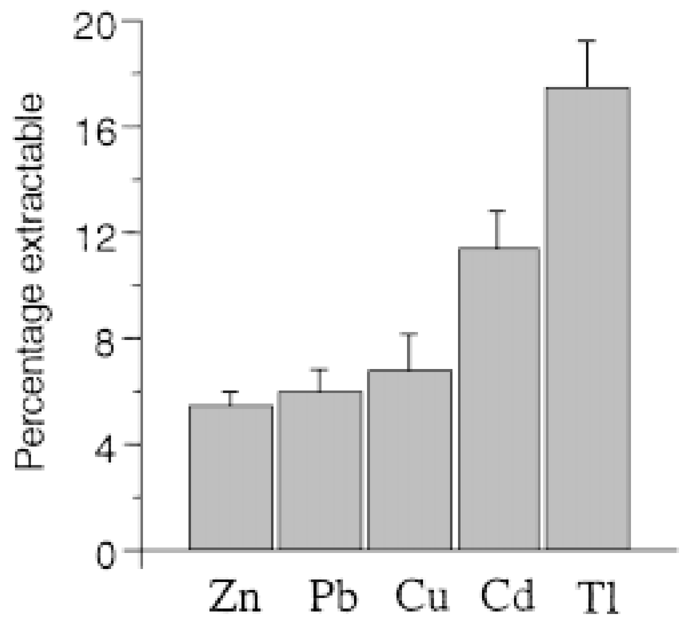

FIGURE 3. Percentage of the total metal concentration in soil that is extractable with 1 *M* ammonium acetate.

efficients (BAC = plant/soil concentration quotients) for thallium in *B. laevigata* and *I. intermedia* (respectively 20.2 and 29.4) make them ideal candidates for the phytoremediation of thallium-contaminated soils. Experiments by Leblanc *et al.* (1999) demonstrated that *I. intermedia* had a fertilized biomass production of around 15 tonnes per hectare per annum. A single crop of this grown on a soil with 14 mg/kg thallium would have a concentration of 411 mg/kg (from Table 1), and thus would remove 6.165 kg of thallium per hectare worth $1850 US at today's prices. Assuming a root depth of 10 cm and a soil density of 1.1, the thallium burden in the top 10 cm of soil would be reduced to 9.2 mg/kg in 1 year.

At present, some sites around the town of St Laurent le Minier are being used for vegetable production. Crop growth is poor, presumably due to the high levels of heavy metals, as well as the general paucity of nutrients in the soil. Additionally, the produce may pose a health risk due to heavy metal contamination — both from plant uptake and wind-borne contamination. Cultivation of hyperaccumulator species such as *I. intermedia* and *B. laevigata* could produce a viable economic return, while decontaminating the soils.

Caution should be exercised in extrapolating the results of these initial experiments to full-scale phytoextraction operations, as it is unknown what the effect of repeated cropping will have on thallium uptake by plants. There was a large variation in the BAC values (3 to 698) for both species, indicating that it may be possible to enhance thallium uptake by altering soil conditions or by selective breeding, a fertile area for future research.

IV. CONCLUSIONS

The thallium uptake of *I. intermedia* and *B. laevigata* is primarily dependent on the concentration of soluble thallium in the soil. As the percentage of total thallium that is soluble is relatively high compared with other metals, fewer problems should be encountered during a thallium phytoextraction operation, particularly when the total concentration of this element in the soil is low. Problems in other phytoextraction operations involve maintaining sufficient plant uptake as the soluble fraction of the target metal in the soil decreases. The current very high world price of thallium metal implies recouping much or all of the costs of phytoremediation by the sale of the harvested biomass, or even giving an overall profit. Future work should focus on the enhancement of thallium uptake by these species, and on agricultural practices required for efficient crop production of them.

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REFERENCES

Anderson, C. W. N., Brooks, R. R., Chiarucci, A., LaCoste, C. J., Leblanc, M., Robinson, B. H., Symcock, R., and Stewart, R. B. 1999. Phytomining for nickel, thallium and gold. *J. Geochem. Explor.* (in press).

Brooks, R. R., Lee, J., Reeves, R. D., and Jaffré, T. 1977. Detection of nickeliferous rocks by analysis of herbarium specimens of indicator plants. *J. Geochem. Explor.* **7,** 49–57.

Brooks, R. R. 1998. *Plants That Hyperaccumulate Heavy Metals: Their Role in Archaeology, Microbiology, Mineral Exploration, Phytomining and Phytoremediation.* Wallingford, CAB International.

Brooks, R. R., Chambers, M. F., Nicks, L., and Robinson, B. H. 1998. Phytomining. *Trends Plant Sci.* **3,** 359–362.

Chaney, R. L. 1983. Plant uptake of inorganic waste constituents. In: *Land Treatment of Hazardous Wastes,* pp. 50–76. (Parr, J. F., et al., Eds.). New York, Noyes Datya Corp.

Ernst, W. H. O. 1996. Bioavailability of heavy metals and decontamination of soils by plants. *Appl. Geochem.* **11,** 163–167.

Kurz, H., Schulz, R., and Rîmheld, V. 1997. Phytoremediation of thallium and cadmium from contaminated soils — possibilities and limitations. *Proc. Int. Sem. Use Plants. Environ. Remed. Council for Promotion of Utilization of Organic Materials* (ed.), Tokyo, Sept. 1997, 120–122.

Kurz, H., Schulz, R., and Rîmheld, V. 1999. Selection of cultivars to reduce the concentration of cadmium and thallium in food and fodder plants. *J. Plant Nutr. Soil Sci.* **162,** 1–6.

Leblanc, M., Robinson, B. H., Petit, D., Deram, A., and Brooks, R. R. 1999. The phytomining and environmental significance of hyperaccumulation of thallium by *Iberis intermedia* from southern France. *Econ. Geol.* **94,** 109–114.

Robinson, B. H., Brooks, R. R., Howes, A. W., Kirkman, J. H. and Gregg, P. E. H. 1997. The potential of the high-biomass *Berkheya coddii* for phytoremediation and phytomining. *J. Geochem. Explor.* **60,** 115–126.

Robinson, B. H., Leblanc, M., Petit, D., Brooks, R. R., Kirkman, J. H., and Gregg, P. E. H. 1998. The potential of *Thlaspi caerulescens* for phytoremediation of contaminated soils. *Plant Soil.* **203,** 47–56

Tremel, A., 1996. Transfer du Thallium du Sol vers la Plante. PhD Thesis, Université de Nancy.

Waitz, M. F. W. and Percival, H. J. 1993. *Sorption Behaviour of Copper, Lead, Zinc and Cadmium in Three Heavy-Metal-Amended Soils Using* $CaCl_2$ *Extracts and Soil Solutions.* Publication of Landcare Research, Lower Hutt, New Zealand.

Zitco, V. 1975. Toxicity and pollution potential of thallium. *Sci. Total Environ.* **4,** 185–192.

Zyka, V. 1970. Thallium in plants from Alsar. *Sb. Cesky Geologicky ved. Technol./Geochem.* **10,** 91–95.