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

Cher LaCoste,1 Brett Robinson,2,* Robert Brooks,1 Chris Anderson,1 Alessandro Chiarucci,3 and Marc Leblanc4

1Soil and Earth Sciences, Institute of Natural Resources, Massey University, Palmerston North, New Zealand.; 2Horticulture and Food Research Institute of New Zealand, Palmerston North, New Zealand.; 3Dipartimento di Biologia Ambientale, Università di Siena, Siena, Italy.; 4Géofluides-Bassins-Eau, CNRS, Université de Montpellier II, 34095 Montpellier, France.

* Corresponding author; E-mail: r.brooks@massey.ac.nz.

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,
C. LaCoste, et al.

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 Alasar 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 Alasar 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 Biscutella 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
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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 (Figure 1). 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.
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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.

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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.
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<tr>
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<th>Thallium</th>
<th>Lead</th>
<th>Cadmium</th>
<th>Copper</th>
<th>Zinc</th>
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<td><strong>France</strong></td>
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<tr>
<td>I. intermedia</td>
<td>411 (141–1200)</td>
<td>111 (45–278)</td>
<td>9 (3–33)</td>
<td>8 (5–12)</td>
<td>630 (232–1710)</td>
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<tr>
<td>B. laevigata</td>
<td>504 (65–3920)</td>
<td>191 (76–470)</td>
<td>27 (6–121)</td>
<td>7 (4–13)</td>
<td>2290 (805–6530)</td>
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<td><strong>Italy</strong></td>
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<tr>
<td>B. laevigata</td>
<td>492–6</td>
<td>45 (15–130)</td>
<td>4 (1–17)</td>
<td>133 (15–130)</td>
<td>432 (266–699)</td>
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<td>Soil</td>
<td>1 (&lt;1–3)</td>
<td>3791 (2732–5259)</td>
<td>46 (36–60)</td>
<td>683 (34–13808)</td>
<td>19730 (14337–27151)</td>
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Normal plants<sup>a</sup>

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

<sup>a</sup> 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

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<th>pPb</th>
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<th>pH</th>
<th>sTl</th>
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<td>sTl</td>
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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 P < 0.01); S, significant (0.01 P < 0.05); PS, possibly significant (0.05 P < 0.10); NS, not significant (P 0.10).
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/phytoming operations. The high bioaccumulation co-
coefficients (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

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