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Effect of thioligands on plant-Hg accumulation and volatilisation from mercury-contaminated mine tailings

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Abstract

This study investigated the effect of thioligands on mercury (Hg) volatilisation and plant accumulation for *Brassica juncea* plants grown in mine tailings collected from artisanal gold mines in Brazil (the Serra Pelada mine) and China (the Gold Mountain mine). Plants were treated with either $(NH_4)_2S_2O_3$ or NH_4SCN and enclosed in gas-tight volatilisation chambers. Elemental Hg released from substrates was captured in a two-trap system containing 5% $KMnO_4$ dissolved in 2N H_2SO_4. Mercury accumulation was enhanced in the presence of $(NH_4)_2S_2O_3$ for plants grown in GM tailings. There was no significant increase in the plant-Hg accumulation after application of NH_4SCN to the SP tailings. Volatilisation from planted substrates was not affected by the application of thioligands to either GM or SP mine tailings. Mercury volatilisation from planted substrates was significantly higher than from control substrates. Abiotic (photoreduction) and biotic (microbial interactions) factors might be linked to the enhanced plant effect on Hg volatilisation. There was no significant correlation for the Hg mass released from substrates and the amount of Hg uptake by roots and translocated to shoots. Our results indicate that volatilisation and plant-Hg accumulation are two independent processes. Thiosulphate-induced plant-Hg accumulation may be a potential tool for the phytoextraction of Hg contaminated soils but there are risks of groundwater contamination by Hg-containing leachates.

Abbreviations: $(NH_4)_2S_2O_3$ – ammonium thiosulphate; NH_4SCN – ammonium thiocyanate; H_2O_2 – hydrogen peroxide; $KMnO_4$ – potassium permanganate; H_2SO_4 – sulphuric acid

Introduction

Artisanal and small-scale mining (ASM) is characterised by limited planning and the use of simple techniques to extract metals from primary and secondary ore bodies (Hinton et al., 2003). Artisanal mining is a livelihood adopted by rural communities because it represents the most promising source of income. It is, therefore, a central activity to at least 10 million people from the developing world, including emerging economies such as China and Brazil. In general, these small-scale mines have a negative effect on the

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environment, causing deforestation, soil erosion, river diversion and river silting. (Hinton et al., 2003). However, the most profound impact of ASM is the pollution of the environment with metallic Hg (Veiga and Hinton, 2002). It has been estimated that between 450 and 800 tonnes of metallic Hg (i.e., around 20% of total anthropogenic Hg emissions) are released annually into the worldwide environment as a result of artisanal and small-scale gold mining operations. Brazil and China contribute with around 40% of this total (Lacerda, 2003; Veiga, 2004).

Small-scale gold miners are driven by survival and a need to support their family. Consequently, little consideration is paid to the toxic effects of Hg or to the dangerous consequences of Hg release into the environment. Metallic Hg is freely discharged in soils and water in the form of amalgamation tailings that contain up to 500 mg/kg residual Hg (Veiga and Hinton, 2002).

Most Hg that is released into soil is adsorbed onto the solid-phase of organic matter and onto soil minerals, such as sulphides and oxy-hydroxides of iron and aluminium (Evans, 1989). A substantial fraction, however, undergoes physical (leaching, erosion, and volatilisation) and biochemical transformations (methylation, photochemical and biological reduction) (Morel et al., 1998). Mobilisation of Hg can occur through exchange reactions with sulphur-containing ligands and chloride ions, leading to enhanced Hg solubility in soil solution (Schuster, 1991). In weathered tropical soils, Hg bound to iron and aluminium oxy-hydroxides can be mobilised from the surface horizon through the erosion of deforested soils (Roulet et al., 2000). The removal of plant cover allows increased oblique run off on slopes and subsequent depletion of iron oxy-hydroxides and Hg in the upper centimetres of the soil (Roulet et al., 1999). The mobilised Hg eventually forms complexes to dissolved organic constituents and reaches aquatic systems, where it can be exported to areas away from the pollution source (Lacerda and Solomons, 1992; Oliveira et al., 2001; Veiga, 1994). The transformation of inorganic Hg into toxic methyl Hg can occur through the action of methylating bacteria on soluble Hg species (i.e., free Hg ions or Hg complexed to organic acids) under anoxic conditions. Once formed, methyl Hg is biomagnified and, in top predators such as fish, it can exceed safe levels for human consumption (Southworth et al., 2004).

In some scenarios, phytoremediation is a low-cost technology for the remediation of metal-contaminated sites. Plant roots can stabilise a substrate, reduce leaching, and contribute to the build up of organic carbon in soils, thereby rehabilitating degraded land (Robinson et al., 1998). Plants can extract nutrients, accumulate heavy metals and radionuclides, and transform or degrade some organic contaminants (Schnoor et al., 1995). It is, therefore, logical to propose a plant-based system for the remediation of Hg-polluted soils. It has been suggested that terrestrial plants can function both as a source and sink of atmospheric Hg (Leonard et al., 1998a and b; Lindberg et al., 1998, 2002). Further, Hg-phytovolatilisation promoted by Hg-resistant transgenic plants is a promising tool for the removal of inorganic and organic Hg forms from contaminated soils and sediments (Meagher et al., 2000, Heaton et al., 2001, 2003). As an alternative, phytoextraction of Hg from contaminated soils is proposed based on evidence for enhanced Hg accumulation in harvestable plant tissues following substrate treatment with $(NH_4)_2S_2O_3$ (Moreno et al., 2004a). A strategy for Hg removal from low to moderately contaminated soils would involve periodic removal and safe storage of Hg-containing plant biomass after soil treatment with non-toxic chemical solutions. In this work, we aim to investigate the effects of thioligands on plant-Hg accumulation and volatilisation for *B. juncea* plants grown in Hg-contaminated mine tailings. The purpose of this study is focused on the potential use of these plants for the remediation of artisanal gold mine sites in Brazil and China.

Methods and materials

Substrate type

Mercury-contaminated substrates from two locations were investigated in this work: 1) mill tailings collected from the processing centre of the Gold Mountain (GM) mine, North-Central China, and 2) mine tailings collected from the Serra Pelada (SP) artisanal gold mine site, State

of Pará, Brazil (Figure 1). It was requested that the exact location of the GM mine be omitted to protect the local mining community (A.J. Gunson, personal communication). Selected geochemical characteristics of SP and GM substrates are presented in Table 1.

Sample collection

Mine tailings from the SP mine were collected by the first author during a field survey of the mine during June 2003. Tailings from the GM mine were provided by the Department of Mining and Mineral Processing Engineering at the University of British Columbia (UBC), Vancouver, BC, Canada.

Plant growth conditions

Due to the phytotoxic Hg concentration of the original GM mine tailings (Table 1), the plant experiments were carried out in a modified GM substrate. The modified substrate was prepared through dilution of the original GM mine tailings (average concentration of 67 mg/kg, Table 1) with a 1:1 mixture of coarse and fine silica sand (fine fraction < 1000 μm) to give a final Hg concentration of 2.5 mg/kg (Table 1). The levels of Hg found in the collected SP samples were unexpectedly low (average concentration of 0.27 mg/kg, Table 1). Consequently, the plant experiments for this substrate were carried out without dilution. Both substrates were supplemented with Osmocote (slow release NPK fertiliser) at 5 g/kg and left to equilibrate for 1 week prior to seeding. The SP substrate was amended with lime to adjust the pH to 6. No lime was added to the GM substrate as the pH of substrate (around 8) was suitable for plant growth. Plastic pots (7×7 cm) were filled with each substrate and sown with seeds of *B. juncea* at a rate of $\sim$20 seeds per pot ($n = 20$ for each substrate type). Two weeks after germination, each pot was thinned to leave one individual plant. Hoagland's nutrient solution (5 mL of 1/4 strength) (Hoagland and Arnon, 1950) was irrigated onto the pots every second day to supplement the plant's nutritional requirements. Plants were kept in a greenhouse with ambient temperature set to vary

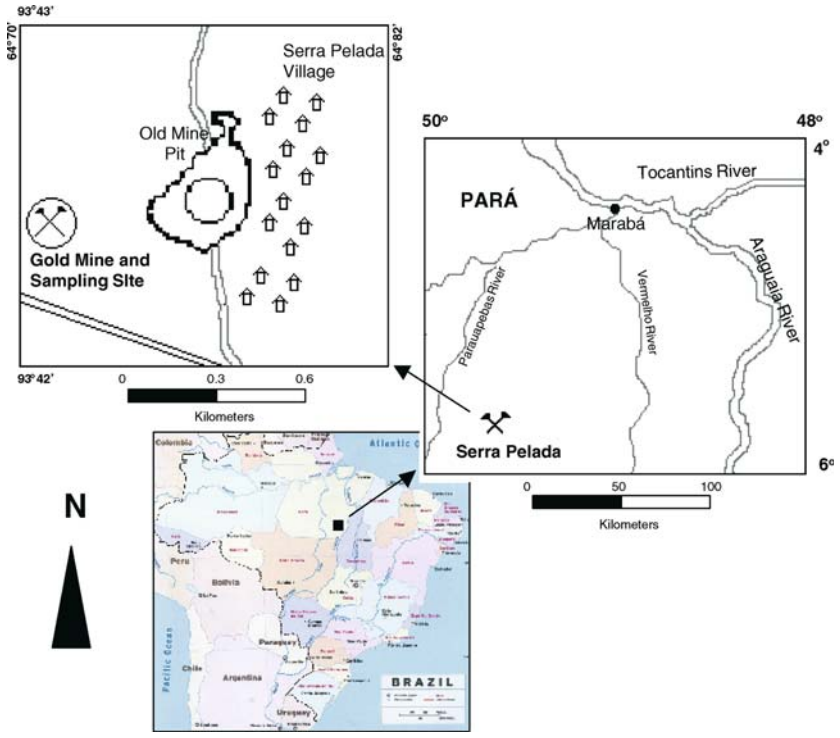

Figure 1. Geographic location of the sampling site and the Serra Pelada artisanal gold mine, State of Pará, Brazil.

Table 1. Selected geochemical characteristics of original and modified[a] Gold Mountain (GM) and Serra Pelada mine tailings

	Tailings type		
	Original GM[b]	Modified GM	Serra Pelada[c]
Total concentration			
Hg (mg/kg)[d]	67.4 (±11)	2.4 (±0.07)	0.27 (±0.06)
Au (mg/kg)	1.58	na	0.09
Cu (mg/kg)	9356	na	1338
Mn (mg/kg)	na	na	188.4
Fe (%)	4.48	na	1.30
Other characteristics			
pH[e]	9.4	8.2	5.4
Eh (mV)[e]	−137	−63	93
Total Carbon (%)[f]	0.7	0.3	0.1
Total Nitrogen (%)[f]	0.07	< 0.01	0.02
OM (%)[f]	1.3	0.5	0.3
C:N	10	> 30	5
Soil Volume (g/ml)[f]	1.42	1.55	1.30

[a]The modified substrate was prepared through dilution of the original GM mine tailings with a 1:1 mixture of coarse and fine silica sand.
[b]Analysis of total Au, Cu, Mn and Fe for the original mine tailings were carried out by ACME Labs, Vancouver, BC, Canada.
[c]Source: Cabral et al., 2002.
[d]Total Hg concentrations in the samples were determined through *aqua-regia* digestions; values are the mean of three replicates ±1 standard deviation.
[e]The pH and Eh values are the mean of three measurements.
[f]Analyses of total nitrogen and carbon, organic matter content and soil volume were carried out by Fertilizer and Lime Research Centre, Palmerston North, NZ.
na = not analysed.

diurnally from 15–25 °C without humidity control. Unplanted substrates for each type of mine tailing were used as controls and were treated in the same way. Pot positions were randomly changed on a periodic basis to equalise light exposure. Daily watering was carried out everyday to field capacity. All the plants were treated before the outset of flowering.

Extractable Hg

Extractable Hg concentrations were determined for the SP and both the modified and original GM tailings substrates. The extractants investigated were ammonium thiosulphate ($[NH_4]_2S_2O_3$) and ammonium thiocyanate supplemented with hydrogen peroxide ($NH_4SCN + H_2O_2$). One gram of substrate was weighed into 50 mL polypropylene centrifuge tubes in triplicate. After addition of extractant solutions (20 mL at 2 g/L, unless otherwise stated), the tubes were rotated in a shaker overnight at 45 rotations per minute (RPM) and the supernatant separated after centrifugation at 3000 RPM for 3 min. The pH and Eh of the extractant solutions were measured using a pH and Eh meter (Copenhagen Radiometer, PHM 83 Autocal pH meter).

Volatilisation and plant-Hg accumulation experiments

Brassica juncea plants growing on each growth substrate were treated either with $(NH_4)_2S_2O_3$ or NH_4SCN at a rate of 2 g of chemical per kg of substrate. After 5 weeks of growth, the effect of plants, thioligands and substrate type on volatile Hg emissions was assessed. Water was used as a comparison to the thioligand treatments. Pots without plants (unplanted pots) were used as controls. Immediately after treatment, both pots and plants were individually enclosed within a gas-tight acrylic volatilisation chamber (3.6 L volume). Volatile Hg released from the soil–plant system was captured in two successive trap

solutions containing 5% $KMnO_4$ dissolved in 2 N H_2SO_4. The efficiency of this trap solution to quantitatively capture Hg has been shown to range from 95% to 99% (Kimura and Miller, 1960). A continuous airflow was supplied to the volatilisation chamber using a small air pump. Mercury vapour released by the plants was driven together with the incoming air into two Erlenmeyer flasks, each containing 70 mL of the acid trap solution. The flow rate of the incoming air was monitored using an air flow meter (J&W, model AMD 1000, California, USA) and was constantly held to 100 mL/min using small clamps attached to the air outlets. The outlet of the second acid trap was open to the atmosphere to maintain pressure equilibrium within the trap system. A 10 mL syringe attached to the volatilisation chamber was used to water the plants during the period of volatile Hg collection. Watering was carefully performed to avoid any possible loss of Hg through leaching. Volatilisation was measured over a 3 days period inside a plant growth chamber with photoperiod set for 14 h and temperature kept constantly at 22 °C. Collection of volatile Hg was done in triplicate for thioligand-treated plants, plants irrigated with water and control pots. The plant growth chamber has a capacity for three individual volatilisation chambers and, therefore, the experiment was repeated three times for each type of mine tailings. At the end of the three-day period, the acid trap solutions were transferred to 100 mL airtight plastic containers and stored at 4 °C until analysis. The precipitated fraction of the acid traps was redissolved using 50 mL of concentrated hydrochloric acid, and the resulting solution was stored using the same procedure. The mass of volatile-Hg collected for each replicate was, therefore, the sum of the Hg readings in the soluble and precipitated fractions of both acid traps. The use of this experimental apparatus has allowed an average Hg recovery of 90% for *B. juncea* plants cultured in Hg-spiked solutions (Moreno et al., 2004b).

Plant harvest

At the end of the experiments, plants were harvested and washed in tap water. Shoots were excised from roots by using a steel blade. The intact root system could be harvested from the pots by soaking the bulk roots with the adhering substrate in a bucket filled with water. The buckets were acid washed and the water was fully replaced after each soaking period. The roots were further washed several times with tap water to remove residual substrate particles. The soaking process was carried out for 1 h and was done separately for each type of substrate and chemical treatment. Plant tissues were placed into individual paper bags and dried at 70 °C. After drying, all plant samples were sealed in plastic bags until Hg analysis.

Plant digestion

Ground shoots and roots were accurately weighed (0.1 g) into 50 mL plastic pots. Concentrated HNO_3 (15 mL) was then added. The digest samples were left overnight and, in the following day, (RO) were heated in a water bath at 100 °C for 1 h. Digest solutions were transferred to 10 mL polythene tubes and diluted with reverse osmosis (RO) water to make a final volume of 10 mL. A blank reagent was used with all digestions.

Substrate digestion

The total mercury concentration was determined through *aqua regia* digestion of dried and sieved (< 1000 μm) SP and GM substrates (original and modified). One gram of substrate was weighed into 50 mL polypropylene pots in triplicate and a 15 mL solution of HNO_3 and HCl at 1:3 ratio was added. The samples were digested in a water bath at 100 °C for 1 h and the filtrates diluted to a final volume of 50 mL using RO water.

Mercury analysis

Total Hg concentrations in plant, substrate digests and in extractant and trap solutions were analysed through the hydride-generation atomic absorption spectrometry technique (Moreno et al., 2004c). The analysis was performed using a GBC 909A atomic absorption spectrophotometer (AAS, Victoria, Australia) operating in the flame mode. A sodium borohydride solution (5% $NaBH_4$ + 1% KOH) in combination with 10 mL of 0.5 *M* of HCl was used to generate the Hg vapour. The limit of detection (LOD) for

mercury in solution was 5 ng/mL. Reagent blanks were below detection limits in the solution. Linear calibration curves were obtained over the range of 125–1000 ng/mL of Hg using four standards prepared from a 10 mg/L mercuric nitrate ($HgNO_3$) spectrosol solution (May & Baker, AAS standard reagent solution, England). Solutions with Hg concentration over the 1000 ng/mL range were diluted with RO water. The Hg readings obtained from the replicate analysis ($n = 10$) of a standard solution containing 1 mg/L of Hg could be reproduced with less than 5% of variation. The analytical method was assessed for quality control by an external certified laboratory and the maximum discrepancy was 15%.

Statistical analyses

In order to study changes in Hg volatilisation as a function of sulphur-containing solutions ($NH_4SCN + H_2O_2$ and $[NH_4]_2S_2O_3$), substrate type (SP × GM) and plants (planted × unplanted substrates), a randomised experimental design was used. The analyses of variance (ANOVA) were performed in single treatments with the following one-way structure: planted/water/SP, planted/$NH_4SCN + H_2O_2$/SP, planted/water/GM, planted/$(NH_4)_2S_2O_3$/GM, unplanted/SP, unplanted/GM. Linear contrasts were then performed for the following comparisons:

(a) Unplanted × Planted (ignoring substrate type and thioligands);
(b) Planted/SP × Planted/GM (ignoring thioligands);
(c) Unplanted/SP × Planted/SP (ignoring $NH_4SCN + H_2O_2$);
(d) Unplanted/GM × Planted/GM (ignoring $[NH_4]_2S_2O_3$);
(e) Planted/$NH_4SCN + H_2O_2$/SP × Planted/water/SP; and
(f) Planted/$(NH_4)_2S_2O_3$/GM × Planted/water/GM.

A copy of SAS PC version 8e was used for statistical analyses (SAS Inst, 1988). Differences between three or more treatment means in the remaining experiments were performed through one-way analysis of variance (ANOVA). Tukey's test was used for pairwise comparison of means at 0.05 and 0.01 significance levels. The *t*-test was performed for comparing two treatment means, assuming equality of variances. Correlation analysis was used to assess the positive and negative dependence between two variables. The normality of the data was assessed through the Shapiro–Wilk test. The ANOVA for testing the effects of plants, thioligands, and substrate type on Hg volatilisation was carried out in log- transformed data.

Results

Total and extractable Hg in substrates

Of the chemical extractants used, NH_4SCN released the highest concentration of Hg from SP tailings (Figure 2). The extracted Hg concentration was not significantly different from the soluble Hg concentration after *aqua regia* digestion (Table 1, $P > 0.05$). Ammonium thiosulphate released the highest concentration of Hg from both the original and modified GM substrate when compared to controls ($P < 0.0001$, Figure 2). The concentration of Hg extracted using $(NH_4)_2S_2O_3$ was greater than that made soluble after *aqua regia* digests for the original samples ($P < 0.01$) but not for the modified substrate ($P > 0.05$, Table 1, Figure 2).

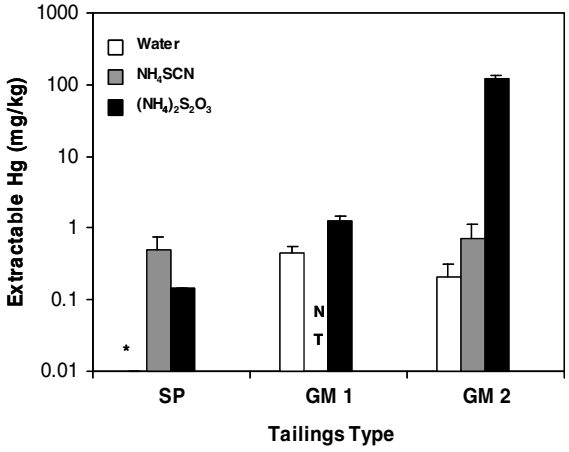

Figure 2. Effect of thioligands (applied at 2 g/kg substrate) on extractable Hg concentrations of Serra Pelada (SP) and Gold Mountain (GM) substrates. Bars denote ± 1 standard deviation from the mean of three replicates. The symbol (*) denotes Hg below detection limits. GM 1 and GM 2 = modified and original GM substrates, respectively. $(NH_4)_2S_2O_3$ = ammonium thiosulphate, NH_4SCN = ammonium thiocyanate supplemented with hydrogen peroxide (H_2O_2) at 0.3%, N T = not tested.

Effect of plants, substrate type and thioligands on plant-Hg accumulation and volatilisation

Table 2 shows the dry weights, plant Hg concentration and the bioconcentration factor for *B. juncea* plants after substrate treatment with either thiosulphate or thiocyanate solutions. The root and shoot biomass was not significantly different between water and thioligand-treated plants for each type of mine tailings. The low levels of soluble Hg in the SP substrate (Figure 2) limited the effect of NH_4SCN on plant-Hg accumulation and no significant differences in Hg values were found between the two treatments ($P > 0.05$, Table 2). However, there was a tendency for increased Hg uptake in the presence of NH_4SCN. This trend was more pronounced for shoot tissues, which concentrated around 2.3 times more Hg than water-treated plants (Table 2). The application of $(NH_4)_2S_2O_3$ to GM substrates increased significantly the Hg accumulation in roots and shoots relative to the water treatment ($P < 0.05$, Table 2). The bioconcentration factor (BF, concentration in plant tissues/concentration in substrates) indicated the superior ability of root tissues to concentrate Hg from both types of mine tailings (Table 2). In the presence of $(NH_4)_2S_2O_3$, this ability was greatly enhanced for roots and shoot tissues, which were able to concentrate between 32 and 17 times the Hg value found in the substrates.

Figure 3 shows the total (a) and extractable (b) Hg concentrations (mg/kg) for the GM substrates at the end of the experiment. Total Hg concentrations in the $(NH_4)_2S_2O_3$-treated substrates were significantly lower than the Hg concentration in the water-treated substrates ($P < 0.05$, Figure 3a). This difference was most pronounced with respect to extractable Hg concentrations ($P < 0.0001$, Figure 3b). This concentration discrepancy is possibly related to the plant uptake of insoluble Hg fraction dissolved after application of $(NH_4)_2S_2O_3$ to the substrates. As there was limited plant Hg uptake from the SP tailings, no significant difference in the total and extractable Hg fractions was observed between water and NH_4SCN-treated substrates ($P > 0.05$) (data not shown).

Table 3 shows the volatile Hg mass captured in the acid permanganate traps for planted (water and thioligand-treated) and unplanted (controls) SP and GM substrates after the end of the experiment. The associated contrasts and their *F*-ratio and *P*-values for these treatments are shown sequentially in Table 4. The presence of *B. juncea* plants significantly enhanced Hg volatilisation relative to controls (unplanted tailings) ($P < 0.0001$, Tables 3 and 4). The mass of volatile Hg released from planted GM substrates was increased by a factor of 12 when compared to unplanted GM substrates ($P < 0.0001$, Tables 3 and 4). In contrast, the mass of Hg emitted from planted SP substrates was not significantly

Table 2. Dry weights, plant Hg concentrations, and the bioconcentration factor (BF) for water and thioligand-treated *B. juncea* plants grown in Serra Pelada and modified GM mine tailings. Values are the means of three replicates ±1 standard deviation. Letters compare treatment means in the vertical for each tailings type. Means with the same letters are not significantly different ($P > 0.05$)

Tailings Type/Treatment	Dry Weight (mg)		Plant Hg (mg/kg DW)		BF[a]	
	Root	Shoot	Root	Shoot	Root	Shoot
SP/Water	48 ± 21 a	171 ± 43 a	0.64 ± 0.3 a	0.08 ± .007 a	2.3	0.29
SP/NH_4SCN[b]	49 ± 15 a	185 ± 37 a	0.74 ± 0.1 a	0.18 ± 0.17 a	2.7	0.66
GM/Water	97 ± 33 a	484 ± 134 a	6.1 ± 3.7 a	BDL	2.5	NA
GM/$(NH_4)_2S_2O_3$[b]	60 ± 14 a	412 ± 143 a	77.6 ± 35 b	41.5 ± 2.7	32	17

[a]The bioconcentration factor was calculated according to the equation: total Hg concentration in plant tissues (mg/kg DW)/total Hg concentration in substrates (mg/kg).
[b]Thioligands were applied at rate of 2 g per kg of substrate; ammonium thiocyanate was supplemented with hydrogen peroxide at 0.3 %.
NH_4SCN = Ammonium thiocyanate; $(NH_4)_2S_2O_3$ = ammonium thiosulphate; BDL = below detection limits; NA = not applicable.

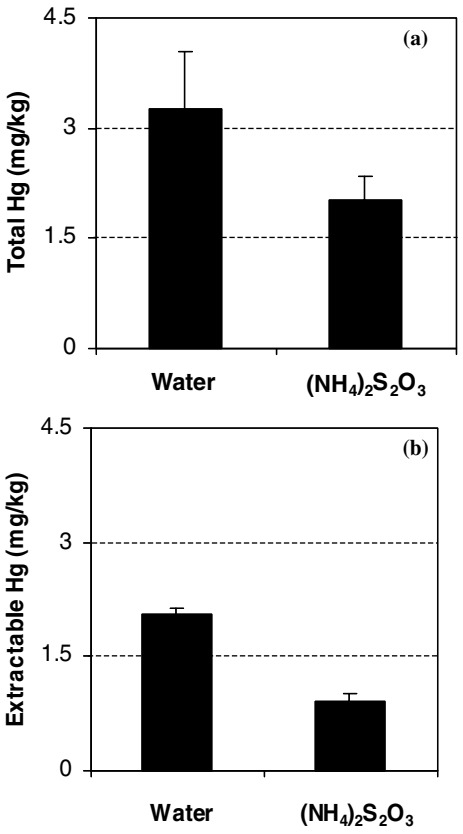

Figure 3. Total (a) and extractable (b) Hg concentrations in Gold Mountain substrates after growth of *B. juncea* plants and application of ammonium thiosulphate at 2 g/kg. Bars denote ± 1 standard deviation from the mean of five replicates. $(NH_4)_2\ S_2O_3$ = ammonium thiosulphate.

different to the Hg mass emitted from unplanted SP substrates ($P > 0.05$, Tables 3 and 4). However, we found a significant plant effect for the Hg mass emitted when water-treated substrates were compared to controls (unplanted) ($P < 0.05$, Tables 3 and 4). In this case, Hg emissions from planted substrates were increased 2.5 times relative to emissions from unplanted SP substrates (Table 3). The Hg mass emitted from planted SP substrates was significantly lower than the Hg mass released from planted GM substrates, suggesting a substrate Hg concentration effect in the volatilisation process ($P < 0.0001$, Tables 3 and 4). The addition of thioligands did not affect significantly Hg emissions from either SP or GM planted substrates ($P > 0.05$, Tables 3 and 4).

The effect of thioligands on Hg mobilisation, volatilisation, shoot accumulation and translocation for *B. juncea* plants grown in SP and modified GM substrates is shown in Table 5. The application of thioligands increased the soluble Hg mass in substrates by a factor of 0.5 to 1.8 without the generation of leachates. The increased soluble Hg fraction induced enhanced root uptake and translocation to shoot tissues (Table 5). This pattern was more evident for plants grown in the GM tailings, where the Hg mass translocated to shoots corresponded to almost 80% of the total Hg mass taken up by the plants (Table 5). By contrast, the application

Table 3. Mercury mass (μg) volatilised from planted and unplanted Serra Pelada (SP) and Gold Mountain (GM) substrates. Planted substrates were treated with thioligands at 2 g/kg (unless otherwise stated) prior to Hg collection in the acid permanganate traps

Tailings Type	Treatment	N[d]	Hg Mass (μg)[a]		Total Hg Mass (μg)[b]
			Trap 1	Trap 2	
	Unplanted	6	0.58 (1/3)	0.10 (1/3)	0.68
SP	Planted/Water	6	1.16 ± 0.87 (3/3)	0.52 ± 0.23 (3/3)	1.68 ± 1.07
	Planted/NH_4SCN[c]	6	0.38 ± 0.17 (2/3)	0.67 (1/3)	0.71 ± 0.65
	Unplanted	6	0.165 (1/3)	BDL	0.16
GM	Planted/Water	6	3.78 ± 2.25 (3/3)	2.86 ± 1.46 (3/3)	6.65 ± 3.67
	Planted/$(NH_4)_2S_2O_3$	6	4.85 ± 1.01(3/3)	1.90 ± 0.57 (3/3)	6.75 ± 0.68

[a]In between brackets are shown the frequency for the detectable Hg mass per number of analysed replicates.
[b]Total Hg mass is the arithmetic mean of three replicates for the Hg mass collected in two acid traps.
[c]NH_4SCN treatment was supplemented with hydrogen peroxide at 0.3%.
[d]N = 3 for each of the traps.
BDL = Hg below detection limits.

Table 4. Linear contrasts and the associated *F*-ratio and *P*-values for the effect of *B. juncea* plants, thioligands and substrate type on Hg volatilisation from Serra Pelada (SP) and Gold Mountain (GM) substrates

Contrasts[a]	DF[b]	F- ratio	Pr > F[b]
Unplanted × Planted	1	38.92	< 0.0001
Planted/SP × Planted/GM	1	34.77	< 0.0001
Unplanted/SP × Planted/SP	1	2.57	0.1257
Unplanted/SP × Planted/Water/SP	1	5.64	0.0336
Unplanted/GM × Planted/GM	1	53.60	< 0.0001
Planted/NH_4SCN/SP × Planted/Water/SP[c]	1	0.95	0.3417
Planted/$(NH_4)_2S_2O_3$/GM × Planted/Water/GM	1	0.00	0.9846

[a]The associated hypothesis for each contrast tested possible differences between the means of single treatments; comparisons were not orthogonal.
[b]DF = degrees of freedom; Pr > F = probability level for rejecting or accepting the hypothesis associated with each linear contrast at the $\alpha = 0.05$ level.
[c]Ammonium thiocyanate (NH_4SCN) was supplemented with hydrogen peroxide at 0.3%.

Table 5. Mercury mobilisation, volatilisation, shoot accumulation, and translocation for water and thioligand-treated *B. juncea* plants grown in Serra Pelada (SP) and Gold Mountain (GM) mine tailings. Letters compare treatments means ($n = 3$) in the vertical for each type of mine tailings. Means with the same letter are not significantly different ($P > 0.05$)

Tailings type/Treatment	Mobilisation (%)[a]	Volatilisation (%)[b]	Root Accumulation (%)[b]	Shoot Accumulation (%)[b]	Translocation (%)[c]
SP/water	BDL	3.10 a	0.046 a	0.012 a	21.21 a
SP/NH_4SCN[d]	180	1.31 a	0.064 a	0.032 a	29.37 a
GM/water	18.44 a	1.71 a	0.13 a	NA	NA
GM/$(NH_4)_2S_2O_3$[d]	52.76 b	1.73 a	1.21 b	4.38	78.31

[a]Mobilisation was calculated according to the equation: Extractable Hg (mg/kg)/Total Hg (mg/kg) × 100. [b]Volatilisation, root and shoot accumulation values were calculated according to the equation: Total Hg mass in traps (μg), roots or shoots (μg)/Total Hg mass (μg) in mine tailings at the beginning of the experiment × 100. [c] Translocation was calculated according to the equation: Total Hg mass in shoots (μg)/Total Hg mass in plants (μg) × 100. [d]Thioligands were applied at rate of 2 g per kg of substrate; ammonium thiocyanate was supplemented with hydrogen peroxide at 0.3%. NH_4SCN = Ammonium thiocyanate; $(NH_4)_2S_2O_3$ = ammonium thiosulphate; NA = not applicable due to shoot Hg values below detection limits.

of thioligands did not cause any increase in the Hg volatilisation from substrates. For instance, the Hg mass volatilised from GM substrates was virtually the same for both water and $(NH_2)_4S_2O_3$-treated plants and corresponded to around 1.7% of the total Hg mass in the substrate. For the SP tailings, there was a reverse trend in the Hg volatilisation, which was evidenced by a lower average value for the Hg mass released from NH_4SCN-treated substrates when compared to the water treatment (Table 5). Furthermore, there was no significant correlation between the volatile Hg mass released from planted SP and GM substrates and the soluble Hg mass taken up by roots and translocated to shoots (Table 6).

Discussion

Speciation and solution geochemistry of Hg complexes in the mine tailings

Schuster (1991) uses an Eh–pH diagram for Hg to indicate that the free metal Hg(0) is a potentially stable form of Hg at pH > 5 under reducing to moderately oxidizing conditions. Table 1 shows that SP mine tailings exhibits moderately oxidising conditions and pH 5.4 whereas GM tailings has a slightly alkaline pH (8.2–9.4) and mild reducing conditions. Mercury dispersed in each of these substrates during artisanal gold mining was likely to be stable in the elemental Hg(0) form. As the vapour pressure of Hg in the elemental

Table 6. Correlation coefficients (r) for the Hg volatilisation from planted Serra Pelada (SP) and modified Gold Mountain (GM) mine tailings as a function of the Hg content (μg) in roots, shoots and plants (roots + shoots). The r-values are the mean of at least five replicates (unless otherwise stated)

Mine tailings/Parameter	Root Hg mass (μg)	Shoot Hg mass (μg)	Plant Hg mass (μg)
SP/Volatile Hg (μg)	−0.24 NS	−0.55 NS	−0.23 NS
GM/Volatile Hg (μg)	−0.22 NS	0.12 NS[a]	−0.12 NS

NS = not significant ($P > 0.05$).
[a]Represents the mean of three replicates

state is high, some Hg fraction might have escaped from the system in the gaseous form. However, given that goethite and manganese oxides are abundant in SP tailings (Cabral et al., 2002) and that Fe accounts for 4.8% of total weight of the GM talings (Table 1), it is likely that another Hg fraction was bound to the solid phase of Fe and Mn oxide minerals. The extraction of Hg from the solid phase of these minerals to the substrate solution might have been, therefore, the result of exchange reactions involving the added sulphur-containing ligands (Figure 2).

Mercury is described as a 'soft metal' and has a tendency to form strong complexes with sulphur-containing ligands (Wallschläger, 1998), including the SCN^- and $S_2O_3^-$ anions. The solution geochemistry of metal–thiocyanate complexes favours stable complex formation under moderately acidic and oxidizing conditions (Bowell et al., 1993). Conversely, stable Hg–thiosulphate complexes are likely to form in neutral to alkaline pH conditions (Wilkinson et al., 1987). The geochemistry of the tested mine tailings (Table 1) suggests, therefore, that Hg will form stable complexes with SCN^- and $S_2O_3^-$ anions present in the soil solution of the SP and GM substrates, respectively.

Origin of plant-Hg emissions from contaminated substrates

The quantitative capture of volatile Hg in the potassium permanganate solution under acid conditions can be written by the following equation:

$$2KMnO_{4(aq)} + 3Hg(0)_{(g)} + 4H_2SO_{4(aq)} \longrightarrow 2MnO_{2(prec)} + 3HgSO_{4(prec)} + K_2SO_{4(aq)} + 4H_2O \quad (1)$$

Since elemental Hg(0) is oxidised by potassium permanganate, then we would presume that the predominant Hg form released from unplanted and planted substrates was the elemental Hg(0) vapour.

The flux of Hg(0) from the foliage as a result of transpiration has been considered as a substantial source of elemental Hg to the atmosphere (Lindberg et al., 1998, 2002). The leaf-to-atmosphere path for Hg(0) has been reported for a number of plant species grown in Hg-contaminated soil including the Brassicas *Lepidium latifolium* and *Caulanthus* sp. (Leonard et al., 1998a, b). However, recent data have shown that Hg(0) fluxes from contaminated soils to the atmosphere are not related to the movement of Hg(0) in the transpiration stream (Greger et al., 2005), but rather to processes happening on the soil surface such as incident light, watering, and surface soil temperature and moisture content (Gustin et al., 2004). Comparison of the Hg(0) flux from unplanted and planted substrates using gas-exchange mesocosmos have indicated reduced Hg(0) emissions from planted substrates in the presence of incident light (Gustin et al., 2004). The authors attributed this reduced effect to soil shading of the leaf canopy. However, our results demonstrated that Hg(0) emissions from planted substrates were significantly superior to the unplanted substrates, thus suggesting a plant-mediated factor in the Hg volatilisation process. We, therefore, propose three main factors for explaining the enhanced Hg (0) emissions from SP and GM planted substrates: (1) watering of planted substrates, (2) variations in soil moisture due to air-H_2O emissions from plants and, (3) bacterial interactions in the rhizosphere of plants.

Pulses of Hg(0) emitted to the atmosphere have been associated with watering events over planted substrates (Gustin et al., 2004). Addition

of water to dry soils can enhance Hg(0) emissions from substrates through desorption of Hg(0) from adhering soil particles and replacement by the H_2O molecule. Soil moisture is another factor implicated in the emissions of Hg(0) from Hg-contaminated soils (Lindberg et al., 1999). The fact that planted substrates received more water than controls (unplanted pots) could, therefore, explain the superior Hg(0) mass emissions recorded from planted SP and GM substrates. The same effect could have been promoted by increased levels of moisture content in planted substrates as a consequence of higher air-H_2O vapour concentrations inside the volatilisation chamber.

Caution should be exercised in neglecting the effect of bacteria on Hg volatilisation from contaminated media. A great percentage of bacteria living in Hg-contaminated environments have Hg-resistant systems, and thus are able to catalyse the enzymatic reduction of Hg(II) to Hg(0) (Barkay et al., 1992; Meagher et al., 2000). Rhizosphere bacteria have been demonstrated to enhance root and shoot accumulation of Hg and Se for the wetland plants saltmarsh (*Scirpus robustus* Pursh) and rabbit-foot grass (*Polypogon monspelienses* [L.] Desf.) (De Souza et al., 1999a). Zayed et al. (2000) and De Souza et al. (1999b) reported that bacteria in the rhizosphere of Indian mustard (*B. juncea*) and broccoli (*B. oleraceae*) can account for between 35% and 95% of plant Se volatilisation, respectively. Additional data supporting the effect of rhizosphere bacteria on Hg volatilisation comes from hydroponics experiments with Hg-exposed plant species enclosed in gastight root and shoot volatilisation compartments (Moreno et al., 2004b; Greger et al., 2005). Quantification of the Hg mass volatilised from both compartments revealed that 95% of the total plant-Hg emissions from a *B. juncea* plant originated from the root system (Moreno et al., 2004b). Further experiments with the addition of antibiotics to Hg-contaminated substrates are needed to confirm this hypothesis.

Effect of thioligands on Hg volatilisation and plant accumulation

In this work, we have showed that addition of $(NH_4)_2S_2O_3$ to GM substrates mobilised non-soluble Hg forms in substrates and caused a substantial increase in the Hg content of shoots when compared to water-treated plants (Table 5). There was marginal evidence for an induced plant-Hg accumulation effect after addition of NH_4SCN to SP substrates ($P = 0.059$, Table 3). Yet, no significant differences were found between water and thioligand-treated plants regarding the amount of Hg mass volatilised from both types of mine tailings (Table 5). The enhanced levels of Hg in shoot tissues in the presence of $(NH_4)_2S_2O_3$ were not significantly correlated to the volatile Hg mass emitted from planted substrates (Table 6). These results, therefore, indicate that Hg volatilisation and plant accumulation are independent processes. Greger et al., (2005) have shown that Hg in contaminated media can be transformed to Hg(0) and released to the atmosphere without passing through the transpiration stream of plants. Our results indicated, therefore, that volatile Hg was emitted from substrates in the elemental Hg(0) form. However, Hg mobilised by $(NH_4)_2S_2O_3$ and accumulated into shoots tissues might be in the form of a Hg–thiol complex.

Implications for the phytoremediation of Hg-contaminated land

In the present study, *B. juncea* plants grown in modified GM substrates were able to concentrate around 17 times the average level of Hg in substrates (2.42 mg/kg) following treatment with $(NH_4)_2S_2O_3$ (Table 2). We have previously reported a bioconcetration factor of around 15 in shoot tissues of $(NH_4)_2S_2O_3$-treated *B. juncea* plants grown in a mine tailings located in the North Island of New Zealand (Moreno et al., 2004a). Also, a bioconcentration factor of 25 was found in shoots of $(NH_4)_2S_2O_3$-treated *B. juncea* plants grown in modified GM substrates contaminated with 3.4 mg/kg of Hg (Moreno et al., 2004d). Hence, thiosulphate-induced plant-Hg accumulation in two distinct types of mine tailings have reported average levels of Hg in shoot tissues of *B. juncea* plants in the range of 40–85 mg/kg. These values correspond to around 400–850 times the average background levels of Hg in plants (0.1 mg/kg) (Kabata-Pendias and Pendias, 2000). The levels of Hg accumulated

into shoot tissues of *B. juncea* plants suggest, therefore, that $(NH_4)_2S_2O_3$ could be used to promote the phytoextraction of Hg from contaminated soils. However, there are risks for groundwater contamination of thiosulphate-mobilised Hg. The Hg concentration in leachates has been shown to rise up to four fold after $(NH_4)_2S_2O_3$ amendment to planted Tui mine tailings (Moreno et al., 2004a). The migration of metal contaminants in the unsaturated zone can be controlled by planting deep-rooted phreatophytic trees in metal contaminated sites, as has been proposed by Robinson et al. (2003). In some scenarios, these high water-use trees can eliminate leaching, thus mitigating the risk of groundwater contamination.

Conclusions

Our research has demonstrated that addition of thioligands to mine tailings can enhance plant-Hg accumulation but not volatilisation. Mercury accumulation in plant tissues was significantly increased through $(NH_4)_2S_2O_4$ treatment of the GM substrate. The plant-Hg accumulation effect after addition of NH_4SCN to SP tailings was not significant, possibly because of the low total Hg concentration in the SP substrate. The volatile Hg mass was significantly higher for planted substrates when compared to the controls (unplanted). This discrepancy could be explained as a result of abiotic and biotic factors. Watering and increased levels of soil moisture might have enhanced photoreduction of Hg(II) to Hg(0) in planted substrates. However, there is the possibility of enhanced Hg(0) volatilisation due to microbial interactions in the rhizosphere of plants. In spite of enhancing Hg translocation to shoot tissues, application of $(NH_4)_2S_2O_4$ did not increase the Hg(0) mass released from to GM substrates. This result indicates that Hg volatilisation and plant accumulation are independent processes. Thiosulphate-treated plants were able to concentrate up to 17 times the total Hg concentration in shoot tissues. Thiosulphate-induced plant-Hg accumulation holds potential for the phytoextraction of Hg contaminated soils. Given the potential for leachate generation, thiosulphate-induced Hg phytoextraction may pose a risk to the environment unless the link to receiving waters can be broken. Additionally, the release of elemental Hg(0) gas is likely to occur under field conditions and strategies for the revegetation of Hg-contaminated mine sites should take into consideration Hg losses from the system through volatilisation.

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