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Release of metals and arsenic from various mine tailings by *Eriophorum angustifolium*

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Abstract Previous investigations have found that plants grown on sulphide-rich mine tailings have phytostabilising effects on acid mine drainage (AMD) by decreasing the pH and preventing the release of metals. The possibility of similar effects on tailings containing other minerals was investigated here. The aim was to examine the effects of *Eriophorum angustifolium* on four water-covered mine tailings with different mineralogy – i.e. the plants' effect on the release of elements from the tailings and the uptake of elements – to reveal if *E. angustifolium* is suitable for phytostabilisation in various tailings. Seeds of *E. angustifolium* were sown in different tailings amended with sewage sludge. Arsenic, Cd, Cu, Fe, Pb and Zn levels in the drainage water and in plant tissues were examined. pH, alkalinity, SO_4^{2-} and organic acid concentrations were measured in drainage water, and redox potential and O_2 levels in the pore water. The effect of *E. angustifolium* on the release of metals from the tailings varied with the composition of the tailings. In tailings with a low buffering capacity and low element and sulphide levels, compared with the other tailings, *E. angustifolium* increased the release of metals, which was shown by the high concentrations of elements and low pH in the drainage water and high concentrations of elements in the shoots, thereby generating a bio-concentration factor (BCF) >1. In tailings with a high concentration of elements, the plants had little effect on the levels of the elements in the drainage water, likely due to the presence of buffering agents in the tailings (added prior to the experiment). In this case, the pH did not decrease in the presence of plants and the shoot BCF was <1.

Keywords *Eriophorum angustifolium* · Organic acids · Phytostabilisation · Redox potential · Water-covered mine tailings

Introduction

Mine tailings may consist of fine-grained sand, which is often a waste product of mining, and contain various minerals. An elevated water table within the tailings is often used to reduce the oxygen intrusion into tailings rich in sulphides (Elander et al. 1998), thereby lowering the oxidation of sulphides and the production of acid mine drainage (AMD) (Lowson 1982; Holmström 2000). Low water tables can be used if an O_2-consuming layer with plants and organic materials is present (Stoltz and Greger 2002). Despite the elevated concentrations of metals in mine tailings, plant establishment is possible, especially if the

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tailings are amended with plant nutrients, such as sewage sludge (Borgegård and Rydin 1989; Stoltz and Greger 2002). Stoltz and Greger (2002) reported that the establishment of the wetland plant species *Eriophorum angustifolium* Honck. on submerged sulphide-rich unweathered tailings reduced the release of metals into the drainage water by maintaining the substrate at a high pH and by plant metal uptake. They also found that the translocation of elements to the shoots was relatively low, indicating that this species may be suitable on for the phytostabilisation of sulphide-rich unweathered mine tailings. In continuation of this line of research, the present study was conducted to investigate whether similar positive effects would be found in tailings with different mineralogy.

The mineralogy of the tailings depends not only on the mineralogy of the ore, but also on the mineralogy of the surrounding rock since the two may be difficult to separate during mining. When sulphides weather, sulphate and protons are produced. Other minerals, such as talc, calcite, dolomite and silicates, consume protons during the weathering process. Thus, the minerals that consume protons may negate the effect of sulphide weathering. Therefore, the production of AMD depends on the relative quantities and weathering rates of the various minerals.

Plants may change the chemistry of the substrate in the rhizosphere by, for example, changing the redox status and pH and by releasing root exudates (Marschner 1995). Wetland plants are known to be capable of changing redox conditions by releasing O_2 from the roots (Armstrong et al. 1992; Brix 1993). This process may mobilise elements that, under reduced conditions, are bound to compounds such as sulphides, among others. The change in substrate pH has a large impact on the solubility of metals (Kelly et al. 1998). Plants may change the pH by causing an imbalance in the uptake of either anions or cations, since either H^+ or OH^- and CO_3^{2-} are released in exchange (Nye 1981; Marschner and Römheld 1983; Villegas and Fortin 2001). Furthermore, it has been suggested that organic acids have the ability to both increase and decrease pH (Jones and Darrah 1994; Marschner 1995), and a decreased pH increases metal release from mine tailings (Burckhard et al. 1995; Wasay et al. 2001). Organic acids have also been found to have an impact on the uptake, translocation and tolerance of elements in plants (Thurman and Rankin 1982; Harmens et al. 1994; Ma et al. 2001), and as plants are able to control the release of organic acids, the same plant species growing in alkaline or acidic soils releases different organic acids (Tyler and Ström 1995). Thus, the effect of plant growth on element release and plant metal uptake may vary in tailings with different chemical properties.

In the study reported here, we examined how *E. angustifolium* affected four water-covered mine tailings with different chemical properties and how the latter, in turn, influenced metal and arsenic (As) uptake by the plant. The aim was to determine if (1) the release of metals in general and As in particular and the pH change caused by plant roots were similar in different tailings, (2) the plant mechanisms that affect the element release varied with the composition of the tailings and (3) the properties of the tailings influenced metal and As uptake by plants. The results would reveal if *E. angustifolium* is suitable for phytostabilisation in different tailings.

The first hypothesis was that *E. angustifolium* affected the release of elements from the various tailings differently due to differences in the chemical properties (e.g. mineralogy, sulphur content, buffering capacity and element concentrations) of the four tailings as well as the varying extent of different plant mechanisms, such as O_2 and organic acid release, by the plants. The second hypothesis was that the different properties of the tailings and their associated drainage waters would affect the uptake of elements by the plants.

Materials and methods

Mine tailings and seeds

Mine tailings were collected from four different mine sites in Sweden, all owned by the Boliden AB Company. The metals mined at the sites are shown as follows: (1) Boliden (copper, gold, zinc, lead, silver); (2) Garpenberg (zinc, lead, copper);

(3) Aitik (copper, gold, silver); (4) Laisvall (lead, zinc, silver). None of the tailings had any visual sign of weathering (i.e., no red-orange colour indicative of ferric iron was visible).

The chemical characteristics of the tailings are shown in Table 1, and the mineralogy and particle size of the different tailings in Table 2. Seeds of *Eriophorum angustifolium* Honck. were collected from an old impoundment at the Boliden mine area, where plants had established naturally. The seeds were stored wet at 4°C until use.

One-litre plastic pots with six holes (Ø = 1 mm) punched in the bottom were used; these were lined with a polyamide fabric (pore size: 25 μm; Sintab, Malmö, Sweden) to prevent the roots of the plants from growing through the holes. The pots were filled with approximately 0.5 l mine tailings (Fig. 1) and placed into similar pots but without holes for collection of the drainage water. A plastic flask (20 ml) punched with four 10-mm holes was placed in the centre of each pot. The flasks had a rubber cap and were enveloped in polyamide fabric (pore size: 25 μm; Sintab) to keep the tailings and roots out. Water could be extracted from the flask, and O_2 and pH could be measured in the pore water. The tailings were allowed to settle for 1 week, and then a 3-cm-thick layer of sewage sludge was added on top of the tailings. The sewage sludge was non-sterile and had a water content of about 75% (by weight). After a week, about 40 germinated seeds were planted in the pots. The controls consisted of three treatments: seeds, no sewage; sewage, no seeds; no seeds, no sewage. There were six replicates of each treatment.

Table 1 Chemical composition (means ± SE) of the mine tailings used in the experiment

Element	Boliden	Garpenberg	Aitik	Laisvall
	(mg kg^{-1} dw)[a]			
Si	115,000	232,000	277,000	426,000
Al	23,000	21,900	84,200	11,200
Ca	15,000	32,400	27,600	4,460
K	4,000	5,700	38,000	7,600
Mg	24,000	94,000	11,600	570
Mn	450	3,500	3,800	90
Na	2,300	930	17,900	360
P_2	300	160	1,800	140
Ti	1,700	600	3,500	760
S	306,000	43,000	13,900	3,800
	(mg kg^{-1} dw)[b]			
As	1,763 ± 274	55 ± 3	7 ± 0	5 ± 0
Cd	28.1 ± 1.1	39.2 ± 1.3	0.3 ± 0.1	22.0 ± 1.1
Cu	849 ± 62	679 ± 17	245 ± 11	7 ± 0
Fe $*10^3$	284 ± 7	61 ± 1	31 ± 0	2 ± 0
Pb	1,972 ± 54	5,411 ± 123	15 ± 5	6,525 ± 153
Zn	8,361 ± 340	9,954 ± 202	92 ± 5	5,365 ± 82

[a] ICP-AES, SGAB Analytica, *n* = 1

[b] AAS, *n* = 6

The tailings were covered with water throughout the experiment (13 months). Pots without sewage sludge had a higher water table, whereby the depths of the cover layer(s) on the tailings were similar (approx. 5 cm) in all pots. The pots were kept in a greenhouse maintained at 18 ± 1°C, a relative humidity of approx. 70% and a 12/12-h (light/dark) photoperiod, with supplementary lighting (Osram Daylight lights, HQI-BT 400 W).

Analyses in pots and drainage water

The pH of the drainage water was measured once a month with a Metrohm-744 pH meter. Dissolved oxygen (oxi-196, WTW) and pH (Metrohm-744) (for adjustment of the redox potential measurements) were measured in the pore water on two occasions, after 6 months into the experiment and at the end of the experiment. On the same two occasions, redox potential (Eh) was measured at two depths of the pots: 4 and 9 cm from the top of the pot (i.e. immediately above the tailings and 5 cm down into the tailings), with the electrode being inserted about 5 cm off-centre. For the redox measurements, a Pt-electrode was made according to Hagris and Twilley (1994), connected with a saturated Ag/AgCl double junction reference electrode (model 90-02; Thermo Orion), in a portable meter (model 290A, Orion). The electrodes were tested in quinhydrone and pH buffers according to Bohn (1971). Based on the pH measurements of the pore water, the redox readings were adjusted to pH 7 (Bohn 1971) and the reference potential (+199 mV) added.

At the end of the experiment, drainage water was collected for the analysis of SO_4^{2-}, alkalinity, metals and As. During the entire experiment the

Table 2 Mineral composition of the tailings used (X-ray diffraction, Department of Mineralogy, Swedish Museum of Natural History, Stockholm, Sweden) and their grain size distributions (Geolab, SWECO VBB AB, Sweden)

Mineral composition			Grain size				
Dominating mineral	Lesser amounts of	Trace amounts of	<0.063 (%)	0.063–0.125(%)	0.125–0.25(%)	0.25–0.5(%)	>0.5(%)
Boliden							
Chlorite Talc Quartz Pyrite	Mica Na-rich Plagioclase Dolomite Sphalerite	Amphibole Chalcopyrite	30	34	26	9	1
Garpenberg							
Talc Quartz Chlorite Mica	Amphibole Dolomite Pyrite Sphalerite Epidote	Potassium Feldspar Na-rich Plagioclase Galena Magnetic pyrite	47	37	13	2	1
Aitik							
Quartz Mica potassium feldspar Na-rich plagioclase	Amphibole Epidote	Chlorite Dolomite	4	18	51	26	1
Laisvall							
Quartz	Na-rich Plagioclase Potassium Feldspar Mica Chlorite		8	15	39	33	5

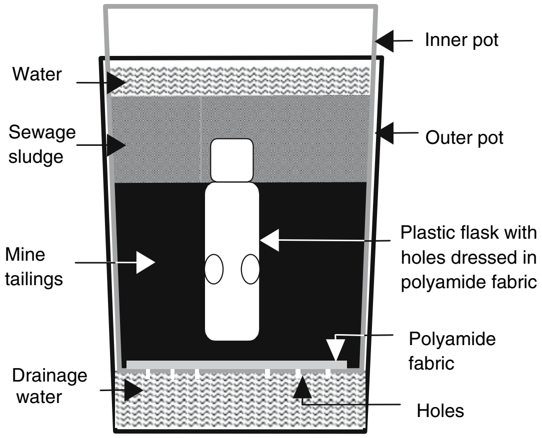

Fig. 1 Experimental set-up in the pots (1 l pots: height = 12 cm, upper Ø = 12 cm, lower Ø = 10)

drainage water was never changed; consequently, at the time of analysis, metals and As had been accumulating for 13 months. The sulphate content of the drainage water was measured by means of a spectrophotometric method modified from Vogel (1961), as described in Stoltz and Greger (2002).

Alkalinity (carbonate alkalinity) was measured by titration of the samples with 0.020 *M* HCl to pH 5.4, according to the European standard EN ISO 9963-2:1995.

For metal and As analyses, 25 ml of drainage water was taken from each pot and treated with 125 µl concentrated HNO_3. The samples were then stored at +4°C until analysed. Metals were analysed by atomic absorption spectrophotometer (Varian SpectrAA-100), applying the flame technique for Fe and Zn, the graphite furnace technique (GTA-97) for Cd, Cu and Pb and the hybrid vapour generation technique (VGA-77) for As. The standard addition technique was used for all metal analyses.

For the analyses of organic acids, fresh drainage water was extracted from the pots with a vacuum pump from below. Each water sample (1.8 ml) was added to 0.18 ml of 1 *M* NaOH to a final concentration of 0.01 *M*, then freeze-dried and stored at –80°C until analysed. Organic acids were analysed in the freeze-dried samples after the addition of 500 μl of redistilled water to each vessel. About 20 μl of the sample was injected manually into the ion chromatograph and run for 20 min in order to obtain a conductivity measurement. A Dionex ion chromatographic system, consisting of a 4,500 gradient pump, an anion micro-membrane AMMS-ICE II suppressor, an ED50A electrochemical detector, a conductivity cell D23 detection stabilizer model DS3-1 and an ionpac ICE-AS6 analytical column (Dionex Corp, Sunnyvale, Calif.). The sample was eluted isocratically with 0.4 m*M* heptafluorobutyric acid, and the flow rate of the eluent was 1.0 ml min^{-1}. The regenerant was 5 m*M* tetrabutylammonium hydroxide with a flow rate of 5 ml min^{-1}. Organic acids (40 mg l^{-1}) were used as standards. This equipment was able to detect the following acids: acetic acid, *cis*-aconic acid, citric acid, D,L-isocitric acid, D,L-tartaric acid, formic acid, fumaric acid, glycolic acid, lactic acid, malic acid, succinic acid and *trans*-aconitic acid.

Analyses of elements in plant tissue and tailings

Plants were removed from the pots and the roots and shoots rinsed in redistilled water, divided into roots and shoots, dried at 80°C and weighed. The plant material was then wet digested in HNO_3:$HClO_4$ (7:3, v/v) and analysed for Fe, Cd, Zn, Cu and Pb with an atomic absorption spectrophotometer (model SpectrAA-100; Varian, Palo Alto, Calif.) using the flame technique. For samples with low concentrations of Cd and Pb, the graphite furnace technique (GTA-97) was used. For As, the hydride vapour generation technique (VGA-77) was used. Reed canary grass (*Phalaris arundinacea* L., reference material NJV 94-4, Swedish University of Agricultural Sciences) was used as plant reference material.

Mine tailings were dried in the same way as plant material and wet digested for 30 min in 7 *M* HNO_3 at 120°C to obtain the firmly bound fraction of heavy metals. The tailings were analysed in the same manner as the plant tissue.

Statistics

Statistical analyses of the data were performed using Simple Regression and ANOVA followed by Post Hoc comparisons with Tukey's Honest Significant Difference (HSD) test to identify differences between the different treatments. Microsoft STATISTICA software was used for all statistical analyses (Statsoft 1999).

Results

Plants in pots without sewage sludge showed poor growth, and there was little difference in all of the measured parameters between the drainage water from this treatment and the two control treatments without plants (data not shown). Consequently, this treatment will not be discussed further.

Alkalinity, pH and SO_4^{2-} levels of the drainage water at the end of the experiment (after 13 months) are shown in Table 3. The addition of sewage sludge increased the alkalinity, while the presence of the plants reduced it in all of the tailings except those from Boliden: the alkalinity in the plant treatments was highest in the Boliden tailings and lowest in the Aitik tailings. Except for the plant-treated Aitik tailings, the pH was between 6.1 and 7.7 in all treated and untreated tailings (Table 3). The pH was stable in the Garpenberg tailings for all treatments during the 13-month experiment (Fig. 2), and a similar pattern was found in the Laisvall and Boliden tailings except for the controls, where the pH increased between 4 and 8 months into the experiment. This pattern was also found in the controls and in the sewage sludge treatment of the Aitik tailings; however at the end of the experiment the sewage sludge treatment showed

Table 3 Alkalinity, pH and sulphate measured in drainage water and redox potential[a] and dissolved oxygen measured in pore water of the pots[b]

Site of tailings and treatment[c]	Alkalinity (mg l^{-1})	pH	SO_4^{2-} (mg l^{-1})	Redox at 4 cm (mV)	Redox at 9 cm (mV)	O_2 (mg l^{-1})
Boliden						
C	160 ± 10 b,x	7.65 ± 0.13 a,x	703 ± 71 a,y	341 ± 11 a,y	65 ± 26 b,z	2.20 ± 0.22 a,x
SS	540 ± 20 a,q	7.53 ± 0.09 a,b,q	131 ± 35 c,r	80 ± 19 b,q	35 ± 37 b,q	1.22 ± 0.31 b,q
SS + *E.a*	480 ± 10 a,k	7.26 ± 0.08 b,k	452 ± 31 b,l	357 ± 34 a,m	213 ± 27 a,m	1.17 ± 0.21 b,k
Garpenberg						
C	180 ± 10 b,x	7.31 ± 0.03 a,x	1,406 ± 44 a,x	369 ± 11 a,y	135 ± 21 b,y	2.23 ± 0.52 a,x
SS	520 ± 10 a,q	7.36 ± 0.08 a,q	1,347 ± 29 a,q	67 ± 23 b,q	100 ± 22 c,q	1.65 ± 0.30 a,q
SS + *E.a*	240 ± 30 b,l	7.07 ± 0.12 a,k	1,265 ± 183 a,k	396 ± 11 a,l,m	276 ± 6 a,m	1.30 ± 0.21 a,k
Aitik						
C	50 ± 30 b,y	6.11 ± 0.31 b,y	211 ± 14 b,z	505 ± 40 a,x	333 ± 17 b,x	1.30 ± 0.12 a,b,x
SS	320 ± 40 a,r	7.02 ± 0.06 a,r	137 ± 43 b,r	72 ± 7 b,q	84 ± 9 c,q	0.97 ± 0.10 b,q
SS + *E.a*	0 ± 0 b,m	3.60 ± 0.07 c,l	507 ± 93 a,l	554 ± 11 a,k	606 ± 34 a,k	1.75 ± 0.15 a,k
Laisvall						
C	120 ± 10 c,x,y	7.27 ± 0.05 a,x	192 ± 15 a,z	342 ± 26 b,y	212 ± 32 b,y	1.92 ± 0.20 a,x
SS	410 ± 20 a,r	7.03 ± 0.06 b,r	57 ± 9 b,r	96 ± 11 c,q	79 ± 21 c,q	1.15 ± 0.13 a,q
SS + *E.a*	290 ± 10 b,l	6.94 ± 0.03 b,k	99 ± 22 b,l	463 ± 13 a,l	454 ± 32 a,l	1.90 ± 0.43 a,k

[a] Redox potential was measured at 4 cm and 9 cm depth

[b] All values are means ± standard error. Different letters in the same column indicate significant differences at $p<0.05$ (Tukey's HSD test): a, b and c within each tailings; x, y and z between controls; q and r between SS treatments; k, l and m between SS + *E.a* treatments

[c] All treatments contained sulphide-rich tailings without or with sewage sludge; treatments with plants also contained sewage sludge. C, Control; SS, sewage sludge; *E.a, Eriophorum angustifolium*,. Each treatment was replicated six times (*n* = 6)

an increased pH (Fig 2, Table 3). Plants grown in the Aitik tailings reduced the pH to 3.6 (Table 3). Sewage sludge decreased the pH slightly in Laisvall tailings (Table 3). In all tailings except those from Garpenberg, sewage sludge decreased the SO_4^{2-} concentration of the drainage water, whereas this decrease was counteracted by the presence of plants in Boliden and Aitik (Table 3).

The redox potential was highest in the Aitik tailings and lowest in the Boliden tailings (Table 3). There was no change in redox potential between the 6-month measurement and the 13-month treatment (data not shown). In general, the addition of sewage sludge reduced the redox potential and the addition of plants increased it at both depths (4 and 9 cm; Table 3). A tendency for this pattern was also found for the O_2 concentration, whereas there were no differences in O_2 levels between tailings. The O_2 concentration in the tailings did not change with time, apart from significant decreases in untreated Aitik and Laisvall tailings, where the O_2 levels were 2.4 mg l^{-1} and 2.8 mg l^{-1}, respectively, after 6 months, decreasing to 1.3 mg l^{-1} and 2.0 mg l^{-1} after 13 months (data not shown).

Of the organic acids in the drainage water, citric acid was present in the highest concentration (10–50 mg l^{-1}), followed by formic acid (1–6 mg l^{-1}) and succinic acid (0.02–0.16 mg l^{-1}). Statistical analyses revealed that the organic acids had no effect on element release.

The highest concentrations of As, Cu and Fe were found in the Boliden tailings, the levels of Cd and Zn were the highest in the Garpenberg tailings and the Pb concentration was highest in tailings from Laisvall (Table 1). Conversely, the lowest levels of As, Cu and Fe were found in tailings from Laisvall and the lowest levels of Zn, Cd and Pb in tailings from Aitik. The sulphate levels were in the order Boliden > Garpenberg > Aitik > Laisvall (Table 1), and the sulphides were assumed to have the same relationship.

The concentrations of As and metals in the drainage water are shown in Table 4. The only effect on As concentrations was found in Boliden

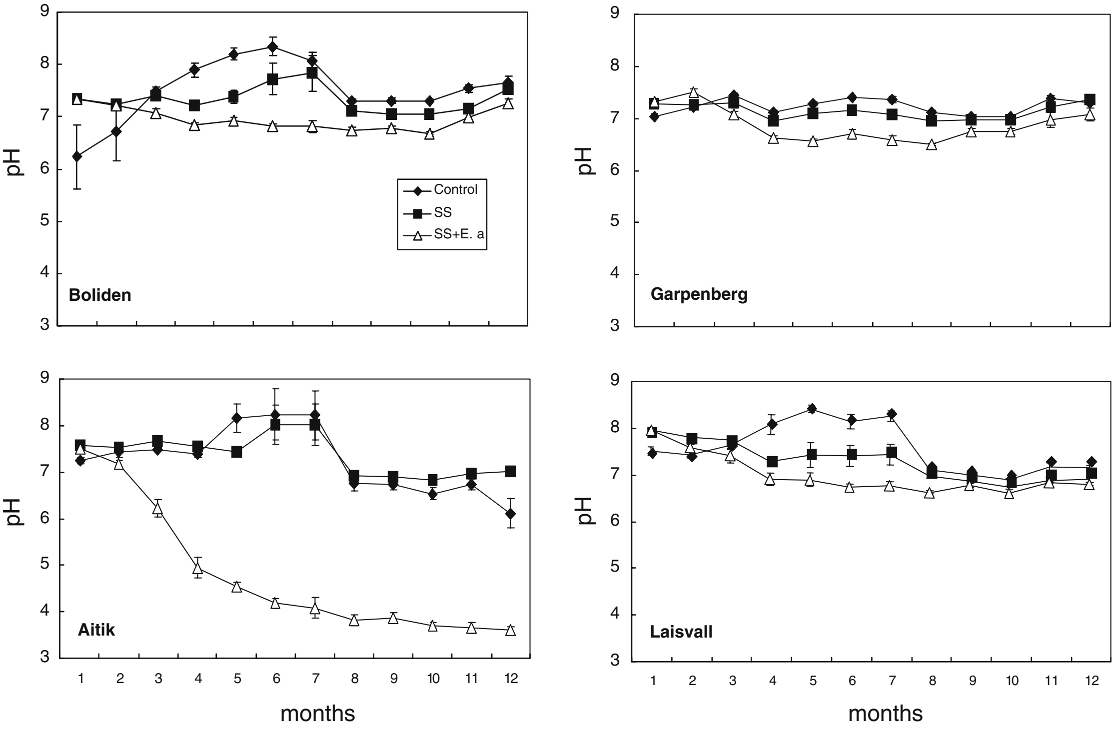

Fig. 2 The pH (mean ± SE) of the drainage water from the tailings, measured once each month during the duration of the experiment

Table 4 Element concentrations in the drainage water from the pots with different tailings and treatments[a]

Site of tailings and treatment[b]	As (μg l^{-1})	Cd (μg l^{-1})	Cu (μg l^{-1})	Fe (mg l^{-1})	Pb (μg l^{-1})	Zn (mg l^{-1})
Boliden						
C	16.0 ± 2.4 b,x	2.0 ± 0.8 b,y	34 ± 4 a,b,y	0.07 ± 0.05 b,y	176 ± 39 a,y	0.8 ± 0.1 b,y
SS	53.6 ± 10.8 a,q	17.0 ± 2.6 a,q	17 ± 2 b,r	2.14 ± 0.36 a,r	227 ± 17 a,r	1.3 ± 0.2 b,r
SS + *E.a*	61.0 ± 16.2 a,k	16.7 ± 3.1 a,k	50 ± 5 a,l	1.56 ± 0.44 a,l	264 ± 14 a,m	3.8 ± 0.4 a,k
Garpenberg						
C	9.7 ± 0.7 a, x,y	32.1 ± 4.1 a,b,x	19 ± 3 b,y	0.31 ± 0.08 b,x.y	2,295 ± 317 b,x	8.4 ± 0.4 b,x
SS	5.0 ± 2.6 a,r	112.8 ± 24.6 a,q	112 ± 59 a,q	0.09 ± 0.03 b,s	4,502 ± 534 a,q	26.2 ± 4.3 a,q
SS + *E.a*	4.9 ± 1.3 a,m	7.2 ± 3.3 b,kl	14 ± 2 b,l	7.36 ± 3.46 a,l	1,777 ± 458 b,l	4.6 ± 0.7 b,k
Aitik						
C	11.1 ± 1.9 a,x,y	1.1 ± 0.2 a,y	125 ± 86 b,x	0.01 ± 0.01 b,y	367 ± 82 a,y	0.1 ± 0.0 b,z
SS	11.8 ± 4.4 a,q,r	2.1 ± 1.1 a,r	135 ± 31 b,q	12.18 ± 3.84 b,q	154 ± 30 b,r	0.3 ± 0.3 b,s
SS + *E.a*	20.8 ± 5.4 a,k,l	4.1 ± 0.6 a,l	2,721 ± 852 a,k	23.25 ± 5.89 a,k	127 ± 12 b,m	1.2 ± 0.2 a,l
Laisvall						
C	8.6 ± 1.7 a,y	2.1 ± 0.7 b,y	34 ± 6 a,y	0.44 ± 0.13 b,x	1,847 ± 507 a,x	0.7 ± 0.2 a,y
SS	8.9 ± 1.7 a,q,r	2.1 ± 0.7 b,r	70 ± 16 a,q	40.19 ± 12.93 a,q	4,413 ± 1042 a,q	0.9 ± 0.2 a,r
SS + *E.a*	7.6 ± 2.1 a,l,m	15.2 ± 4.4 a,k,l	22 ± 12 a,l	5.75 ± 2.12 b,l	3,013 ± 207 a,k	1.6 ± 0.2 a,l

[a] Different letters in the same column indicate significant differences at $p<0.05$ (Tukey's HSD test): a, b and c within each tailings; x, y and z between controls; q and r between SS treatments; k, l and m between SS + *E.a* treatments

[b] C, Control; SS, sewage sludge; *E.a*, *Eriophorum angustifolium*, $n = 6$, means ± SE

tailings, where the addition of sewage sludge increased the As level. The Pb concentration in drainage water was about tenfold higher in drainage water from the Garpenberg and Laiswall tailings than in that from the other tailings in all treatments. The addition of sewage sludge increased the concentrations of Cd and Fe in the drainage water from the Boliden tailings by approximately 20- to 40-fold, the concentrations of Cu, Pb and Zn from the Garpenberg tailings by approximately threefold and the concentration of Fe from the Laisvall tailings by approximately 20- to 160-fold. Sewage sludge decreased the Pb concentration in the drainage water from the Aitik tailings. The presence of plants increased the concentrations of Cu and Zn in the drainage water from the Boliden tailings, the concentration of Fe from the Garpenberg tailings, the concentration of Cu (approx. 5- to 35-fold), Fe and Zn from the Aitik tailings and the concentration of Cd from the Laisvall tailings. Plants reduced the concentrations of Cd (approx.10- to 30-fold), Cu, Pb and Zn (approx. 6-fold) in the drainage water from Garpenberg tailings and the concentration of Fe from Laisvall tailings.

The shoot biomass of *E. angustifolium* was highest in the Aitik tailings, whereas the root biomass in the Garpenberg tailings was significantly higher than that in the Laisvall tailings (Table 5). When plants grown in various tailings were compared, there were no differences in the shoot concentrations of As, Cd, Cu and Fe (Table 5). Plants grown in the Atitik tailings had the lowest shoot concentration of Pb and Zn, while the highest levels of Pb and Zn were found in Laisvall and Garpenberg, respectively. The concentration of As in the root was approximately 50- to 200-fold higher in plants grown in the Boliden tailings than in those grown in the other tailings. The root concentration of Cd was highest in plants from the Garpenberg tailings and lowest in plants from Aitik tailings, with an approximately 21-fold difference between them. The concentration of Cu in the root was lowest (approx. tenfold) in plants grown in the Laisvall tailings, while the concentration of Fe in the root was higher (approx. tenfold) in plants from the Aitik tailings than in those from the Laisvall tailings. The concentration of Pb in the root was lowest (approx. 144- to 270-fold) in plants grown in the Aitik tailings, and the level of Zn in the roots was highest in plants grown in Garpenberg tailings and lowest in plants from Aitik tailings, with about a 16-fold difference.

Figure 3 shows the relationship between the element root concentration (*x*-axis) and the element translocation to the shoot [shoot content:(root + shoot content), *y*-axis] in the four different tailings. The pattern found indicates that when the concentration of an element is low in the root, there is a higher translocation of the element to the shoot.

Discussion

The results of this investigation show that the release of the different elements from each of the four tailings as a result of growing *E. angustifolium* in those tailings was, in fact, different, which is in accordance with the first hypothesis. The reasons for the differences in metal release

Table 5 Dry weight and element concentrations in the shoot and root of *Eriophorum angustifolium* grown in the different tailings with the sewage sludge treatment[a]

	Dry weight (g)	As (mg kg^{-1} DW)	Cd (mg kg^{-1} DW)	Cu (mg kg^{-1} DW)	Fe (mg kg^{-1} DW)	Pb (mg kg^{-1} DW)	Zn (mg kg^{-1} DW)
Shoot							
Boliden	17.8 ± 0.6 b	1.6 ± 0.8 a	2.0 ± 0.3 a	8.9 ± 1.5 a	232.5 ± 85.6 a	16.3 ± 3.4 b	564.7 ± 76.6 b
Garpenberg	21.4 ± 1.7 b	0.5 ± 0.2 a	1.3 ± 0.3 a	7.3 ± 0.3 a	129.4 ± 9.3 a	19.1 ± 2.9 b	832.9 ± 157.5 a,b
Aitik	28.1 ± 2.6 a	0.9 ± 0.2 a	0.7 ± 0.2 a	8.7 ± 1.2 a	126.4 ± 16.1 a	4.0 ± 0.5 c	272.6 ± 21.5 c
Laisvall	17.6 ± 1.0 b	0.5 ± 0.1 a	1.0 ± 0.1 a	8.0 ± 1.0 a	103.3 ± 21.2 a	72.8 ± 7.2 a	531.0 ± 96.1 b,c
Root							
Boliden	11.8 ± 1.0 x,y	281.3 ± 44.1 x	6.2 ± 0.5 y	115 ± 20 x	1,453 ± 159 x,y	1,531 ± 285 x	1,040 ± 101 y
Garpenberg	15.8 ± 0.9 x	4.0 ± 1.0 y	28.0 ± 2.3 x	101 ± 11 x	3,204 ± 1335 x,y	1,301 ± 282 x	2,210 ± 187 x
Aitik	14.7 ± 2.8 x,y	3.1 ± 0.6 y	1.3 ± 0.3 z	143 ± 4 x	6,068 ± 1379 x	9 ± 2 y	137 ± 15 z
Laisvall	8.8 ± 1.0 y	2.3 ± 0.2 y	5.7 ± 1.1 y	14 ± 3 y	695 ± 141 y	2,418 ± 375 x	801 ± 71 y

[a] All values are means ± SE, $n = 6$. Different letters in the same column indicate significant differences at $p<0.05$ (Tukey's HSD test) between the plants grown in the different tailings: a, b and c for shoots and x, y and z for roots

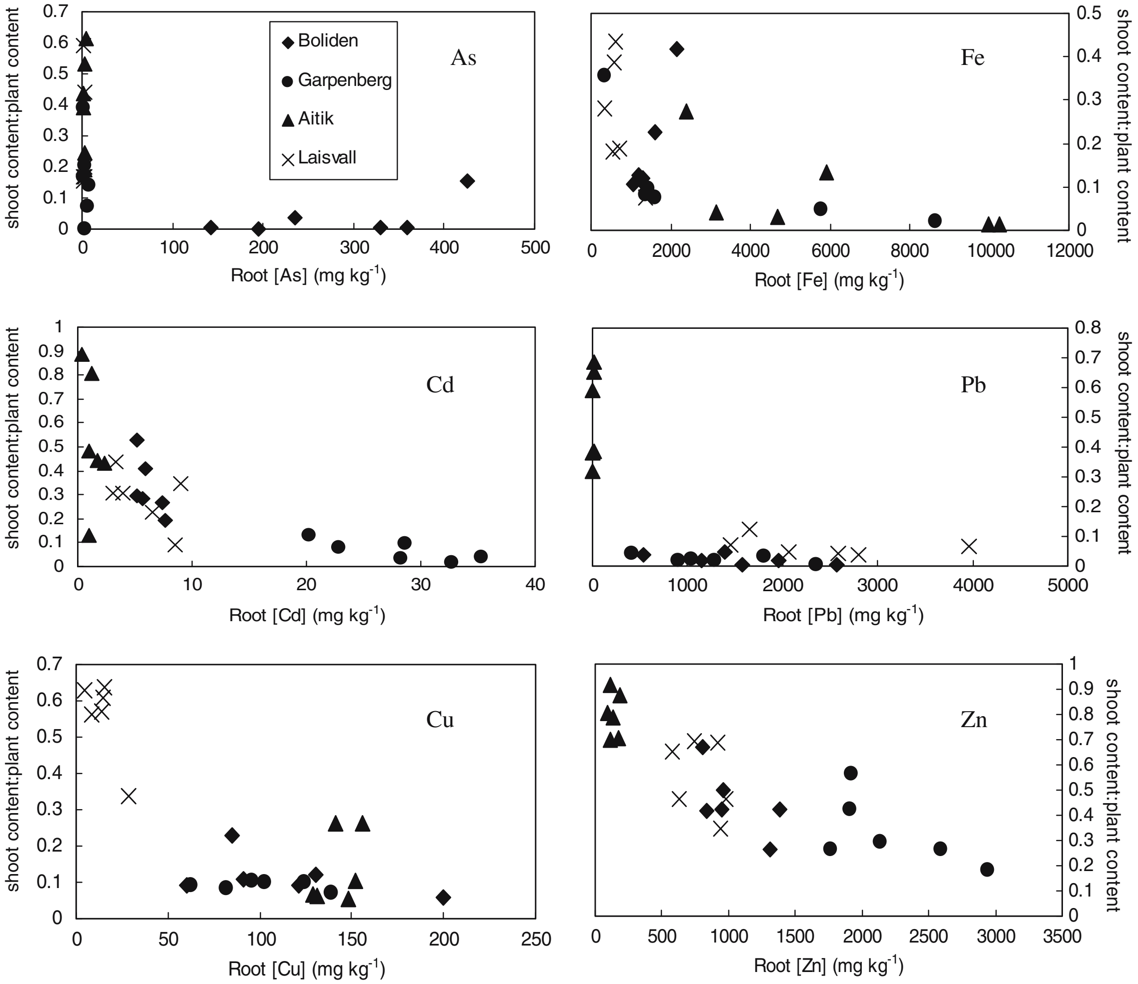

Fig. 3 The relationships between the relative shoot element content and root element concentration

between the tailings were in most cases found to be due to the change in redox potential, probably caused both by the diffusion of O_2 from the plant roots and the mineralogy of the tailings. Organic acids had little effect on the release of elements from the tailings. The fact that the Boliden tailings had been treated with buffering agents (slaked lime) and bactericide was not known at the start of the experiment, but this treatment had a great impact on the tailings since they reduced weathering and element release and kept the pH high (Gleisner 2001).

A previous study (Stoltz and Greger 2002) found that the presence of plants reduced the release of elements from sulphide-rich tailings with a low buffering capacity, primarily because the plants maintained a high pH. In the present study, the presence of plants increased the release of elements from sulphide-rich tailings with a high buffering capacity, such as those from Boliden, by increasing the redox potential as oxygen diffused from their roots (Tables 4 and 5). Increased Zn release from tailings with a high pH has been found for *Typha latifolia*, probably due to root oxygen release (Wright and Otte 1999). A similar effect was seen in tailings with low sulphide levels (Laisvall and Aitik). In the Aitik tailings, the increased concentrations of Cu, Fe and Zn in the drainage water mediated by *E. angustifolium* was probably due to the weathering of chalcopyrite ($CuFeS_2$) and sphalerite (ZnS) (Tables 4 and 5), as both of these minerals are common in Aitik tailings (Strömberg and Eriksson 1996) even though they were not found in the X-ray diffraction analysis (Table 2). The presence of these sulphides is indicated by the decrease in alkalinity, pH and the increase in SO_4^{2-} levels (Table 3).

The pH and the buffering capacity of the tailings have a large impact on the release of metals, since metals are bound to particles (inorganic or organic) or precipitate at high pH (Schnoor 1996). This may be seen in the Garpenberg tailings, which have a relatively high sulphide content but also large amounts of buffering minerals, such as talc, chlorite and dolomite (Tables 1 and 2). In tailings with this kind of mineralogy – i.e. high element and sulphide levels but also high proton-consuming minerals – it is not certain that acidity will ever be generated. If that is the case, plants will probably not have any particular effect on the release of elements over an extended time course. The high and stable pH of the drainage water (Fig. 2) was probably the reason why *E. angustifolium* either reduced – or had no effect on – the elemental content of the drainage water from Garpenberg tailings, with the exception of Fe, for which the levels were increased (Table 4). One possible explanation for the reduced elemental content of drainage water in the presence of plants is the uptake of soluble species by plant roots.

The Boliden tailings, with the highest sulphur levels (Table 1), were expected to generate the most acidity through sulphide oxidation. However, this was not the case, as the pH was above 7 in all treatments and alkalinity was high (Table 3, Fig. 2). This condition was probably due to the fresh Boliden tailings being treated with buffering agents and bactericide, which prevented the oxidation process (Gleisner 2001). In addition, these tailings contain relatively high contents of chlorite, talc and also some silicates (Table 2) that consume protons when weathering. Thus, the positive effects of plant growth found in an earlier study (Stoltz and Greger 2002) – i.e. higher pH and lower metal concentrations in treatments with plants than in those without – could not be seen here since the tailings did not weather.

Even though Aitik tailings, with relatively low sulphide levels, contained some proton-consuming minerals (Tables 1 and 2), the concentrations were not high enough to prevent the pH decrease in these tailings with plant treatment (Fig. 2). The fact that the drainage water of Aitik tailings with plants had the highest Cu and Fe concentrations indicates that the proportion of weathered tailings was high and that the tailings had a low buffering capacity since the lowest alkalinity and pH were found here (Tables 4 and 5). The high weathering could be explained by the high redox potential, which could be due to the relatively large grain size of the Aitik tailings (Tables 2 and 3). The pH stabilising and metal-reducing effect of plants found in sulphidic tailings by Stoltz and Greger (2002), which was probably a protective mechanism to reduce the metal concentrations of the drainage water, was not found in the Aitik tailings. The absence of this mechanism may have been due to the concentrations of elements both in the tailings and in the drainage water that accumulated over a certain time being lower in the Aitik tailings than in water from Kristineberg tailings used in the previous study (Stoltz and Greger 2002). Thus, the environment of the Aitik tailings was less harmful to the plants than that of the Kristineberg tailings, and a mechanism to increase the pH, which reduced the mobility of metals, was not induced. In tailings with relatively low sulphide and element levels and also a low buffering capacity, plants will increase the weathering of the tailings and the release of elements, and no phytostabilising effect on the element will be seen. It should be noted that *E. angustifolium* tolerates a pH range between 2.6 and 10.9 (Nixdorf et al. 2001; Stoltz and Greger 2002), suggesting that there is no toxic pH effect on the plants in the Aitik tailings.

The plants respond differently in the tailings with different chemical properties by changing the pH, and since the pH has a great impact on element speciation, the uptake of the element by the plant will be affected in accordance with the second hypothesis. Concentrations of metals and As in plant roots showed a better correlation with concentrations in the tailings than with their associated drainage waters (not shown, multiple regression, STATISTICA).

The presence of plants did not appear to affect the As concentrations of the drainage waters, thereby confirming previous findings (Stoltz and Greger 2002). The differences in the release between metals and As are probably a reflection of differences in chemical properties, such as anion formation and the fact that As is more mobile under reduced conditions [As (III)] than in aerated conditions [As(V)] (Masscheleyn et al. 1991; Sracek et al. 2004).

Even though the concentrations of elements in the root were influenced by the chemical properties of the tailings, as suggested in the second hypothesis, the concentrations of As, Cd, Cu and Fe in the shoots of the plants did not differ (Table 5). Consequently, the shoot BCF (bio-concentration factor, element concentration in shoot:element concentration in tailings) of *E. angustifolium* varied. For example, the shoot BCF was >1 in the Laisvall tailings for Cu, and in the Aitik for Cd and Zn, while in the other two tailings, which contained relatively higher concentrations of elements, the shoot BCF was always lower than 0.08 (calculated from Tables 1 and 5). The same results have been found for *E. angustifolium* and Zn; a soil with a low Zn concentration resulted in a higher concentration of Zn in the shoots than in roots, while in tailings with high Zn levels the opposite was found (Matthews et al. 2004). This shows that, from the view of shoot concentration, *E. angustifolium* may be suitable for phytostabilisation in some tailings but not in others, since plants used for a phytostabilising purpose should have a low shoot BCF to reduce the distribution of elements to the environment. The difference in translocation can be viewed in Fig. 3: in a plant with a low concentration of the element in the roots, i.e. grown in tailings with low levels that element, there is a relatively higher translocation to the shoot compared with plant grown in high concentrations of the element.

In conclusion, the effects of *E. angustifolium* on the release of elements from mine tailings vary with the chemistry of the tailings. We found no phytostabilising effects of the elements in the drainage water. However, the concentrations of elements in the shoots were lower in relation to the levels in the tailings when the tailings had high levels of those elements, i.e. BCF <1.

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