Vegetation of historical mine waste from the Ljusnarsberg deposit with *Agrostis capillaris* – Impact on leaching of copper

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Abstract In Sweden there are hundreds of sites that need to be remediated due to high release of metals such as Cu. In order to minimize costs the methods should involve cheap materials and technical solutions. This study focuses on the possibility to establish *Agrostis capillaris* on sulfidic mine waste, after mixing with 30 % bark compost, and the subsequent release of Cu. Initially the substrate produced leachates with pH 3.5 containing approximately 1 mg/L Cu. After 4 months the pH had increased to 4.5 and up to 80 % of the Cu was retained.

Keywords *Agrostis capillaris*, bark compost, mine waste, copper, Cu

Introduction

In Sweden hundreds of historical mine waste sites exceed national standards for the release of toxic metals to the environment (SEPA 2013). Most of the sites are relatively small and often located in remote areas. At many sites the metal content in the waste exceeds what is today classified as ore and the waste material is often rich in elements that had no value at the time of mining. Since many of the mines were closed more than 100 years ago there is rarely an identifiable owner. Instead, the ownership of the sites is transferred to the local municipality, which then becomes responsible for the remediation. Therefore the remediation strategy for such sites must be cost efficient (*i.e.* low initial and maintenance costs). Hence, traditional techniques, such as dry or wet covers and water treatment plants, are not feasible solutions at the majority of the sites. Several passive techniques are attractive options for stabilization and water treatment. By establishing a vegetation cover it is possible to lower the erosion from wind, rain and frost as well as reducing the volume of infiltrating rain water (Yang *et al.* 2010). In the case of mine waste this may decrease the release of metals. However, physical and chemical properties of many historical mine waste materials do not promote plant growth due to low nutrient content, coarse structure, low pH and high content of soluble phytotoxic elements (*e.g.* Cu). To overcome these growth-limiting factors, different kinds of additives can be used that either specifically affect one factor (*e.g.* addition of fertilizers to provide more nutrients) or a combination of them (*e.g.* addition of alkali to increase the pH and precipitate metals as insoluble hydroxides). To decrease the cost of the remediation it is of interest to find cheap materials that preferably combine these properties. One candidate material is bark compost since it increases the water holding capacity and also acts as a buffering agent for acid generated during sulfide weathering. The bark also serves as an effective adsorbent for many different metals, including Cd, Cu and Zn, within quite a wide pH range (Reddy *et al.* 1997, Seki *et al.* 1997, Gichangi *et al.* 2012). It is also very essential that the chosen plant species are suitable for these harsh environments. One species that has shown good tolerance against drought, low pH and high metal concentrations is *Agrostis capillaris* (Common bent; Cotter-Howells and Caporn 1996, Banásová *et al.* 2006, Bech *et al.* 2012). In order to improve the establishment of the plants as well as their long term survival addition of species specific mycorrhiza is beneficial or even necessary (Turnau *et al.* 2008).

Here we report some results on the release of phytotoxic Cu when historic sulfidic mine waste is mixed with bark compost (30 %, volume) in order to improve the growth conditions for A. capillaris. The study includes data from two seasons with outdoor pot experiments as well as a general characterization of the materials. The effects on Cu mobilization by addition of mycorrhiza, alkaline material and an easily accessible carbon source are also included.

Materials & Methods

Weathered sulfidic mine waste older than 150 years was collected at the Ljusnarsberg mine site in south central Sweden in late June 2011. Eighteen month before, the mine waste was sieved and material larger than 5 mm was discarded. To enhance the water holding capacity, commercially available bark compost (< 20 mm in size) was added (30 % volume). To estimate the water-soluble fraction of Cu in the mine waste and the bark compost, respectively, a conventional leaching with 18.2 MΩ water was performed at a liquid to solid ratio (L/S) of 10 in an overhead shaker for 24 h at room temperature.

Before filling of the pots, the mine waste and bark compost were thoroughly mixed with garden forks to a test substrate. After mixing, 1.8 L of the substrate was put on top of a 3 cm layer of granite gravel, 10 mm in diameter, in 2 L plastic pots (diam. 180 mm, height 160 mm) and they were gently tapped to compact the mixture. The treatments that were evaluated, according to table 1, were prepared in triplicates. The mycorrhiza culture was kindly provided by Prof. K Turnau (Jagiellonian University in Krakow, Poland). For reference purposes dead mycorrhiza was prepared by heating a sub-volume of the mycorrhiza culture. Water works granules (WWG) were used as an alkaline additive. They are a spherical (diam. 1–4 mm) refuse from softening of potable water and consist of a calcium/magnesium carbonate matrix with varying concentrations of other carbonate forming elements. As an easily accessible carbon source for heterotrophic microorganisms, aspen (*Populus tremula*) wood shavings (AWS) were added to one series. Mycorrhiza (living or dead) as well as WWG were mixed into the top 50 mm whilst AWS was mixed into the entire volume of the substrate. Mycorrhiza, WWG and AWS equivalent to 0.3 L m^{-2}, 0.5 kg m^{-2} and 50 L m^{-3}, respectively, were added.

After preparation of the pots, 40 mL m^{-2} of *A. capillaris* seeds was spread on top of the substrate. No seed cover was used and the pots were immediately sprayed with collected rainwater, equivalent to 10 mm rainfall. After 3 weeks of growth, 2 of the pots from T7 received a single dose of commercial inorganic fertilizer. After hibernation 40 mL m^{-2} of new seeds were spread on each pot to compensate for any loss of plants due to an unusually long period with repeated freezing and thawing during the early part of the winter.

During the first season the pots were watered with rainwater (collected as well as as

Treatment	*Mycorrhiza*		WWG	AWS
	living	dead		
T1	—	—	—	—
T2	—	—	Yes	—
T3	—	Yes	—	—
T4	Yes	—	—	—
T5	—	Yes	Yes	—
T6	Yes	—	Yes	—
T7	—	—	—	Yes

Table 1 *Design of the treatments with living and dead mycorrhiza, water works granules (WWG) and aspen wood shavings (AWS).*

rainfall), equivalent to 10 mm rainfall, every week and samples of the percolation water were collected. During the second season only natural rain falls were used to generate leachates, and sampling took place less frequently. After sampling were the solutions immediately frozen (-20 °C) to maintain their composition. After thawing, pH and electrical conductivity were measured in unfiltered samples. Solutions for Cu and total organic carbon (TOC) analysis were, prior to analysis, filtered through 0.20 µm polypropylene filter disks. Copper was measured by ICP-MS (Agilent 7500 cx) with 10 µg/L Rh as an internal standard and TOC analysis was performed with a Shimadzu TOC-VPH analyzer. For modeling of the aqueous phase Visual Minteq (ver. 3.0) was used.

Results & Discussion

No significant (*p* 0.05) difference in germination was found between the treatments and approximately 90 % of the seeds gave seedlings. After 2 weeks of growth there was no significant (*p* 0.05) difference in shoot length between the treatments. After the snowmelt and in the beginning of the second season the length of the shoots were re-measured and it was found that addition of WWG (T2, T5 and T6) promoted growth, or at least sustained it, (*p* 0.05). Among these treatments, addition of WWG and living mycorrhiza (T6) gave the longest shoots (p 0.05). Even longer shoots (*p* 0.05) were found in the two pots from T7 that received inorganic fertilizer which is clear evidence that the concentration of available nutrients limited the growth in the other treatments.

After leaching of the mine waste with 18.2 MΩ water, an average of 8900 µg/L Cu was found in the solutions (n = 3). The corresponding concentration for the bark compost was 9 µg/L. Compared with the CCME (Canadian Council of Ministers for the Environment) "water quality guidelines for the protection of aquatic life" (CCME 2013) the leachates from the mine waste exceeded the guidelines by more than tree orders of magnitude. The results clearly show that the mine waste is a severe environmental threat. They also indicate that the contribution of Cu from the bark compost in the substrate is of minor importance, even negligibly. In the pot experiments the systems reached an L/S of approximately 5 after the first season and by the end of the second season it had increased to almost 10. During this period the Cu concentration in all leachates (table 2) was only some 20 % of those in the L/S 10 leaching of mine waste which indicates retaining properties of the bark compost as well as the additives. All treatments followed the same decreasing trend during the first season, illustrated in Fig. 1 with data from T1 (reference system). At the end of the first season, reduction factors of 2 to 5 were obtained for Cu in the leachates from the different treatments (table 2). During the second season all treatments produced leachates with slightly increased Cu concentrations.

In T2 and T7 the highest initial concentrations of Cu were observed and also the highest reduction with time (table 2). Over the two seasons the total reduction was as for the first season highest in the treatments that gave the highest initial concentrations (table 2). Addition of WWG (T2) or AWS (T7) resulted in a

Sampling	T1	T2	T3	T4	T5	T6	T7
Initial 07/02/11	933	1321	663	939	1108	823	1919
Final 11/20/11	371	330	327	440	362	248	408
Season 2 average	416	567	488	673	689	418	787
Reduction season 1	2.5	4.0	2.0	2.1	3.1	3.3	4.7
Reduction season 1+2	2.2	2.3	1.4	1.4	1.6	2.0	2.4

Table 2 *Initial and final Cu-concentrations (µg/L) in leachates from all treatments and calculated reduction factors.*

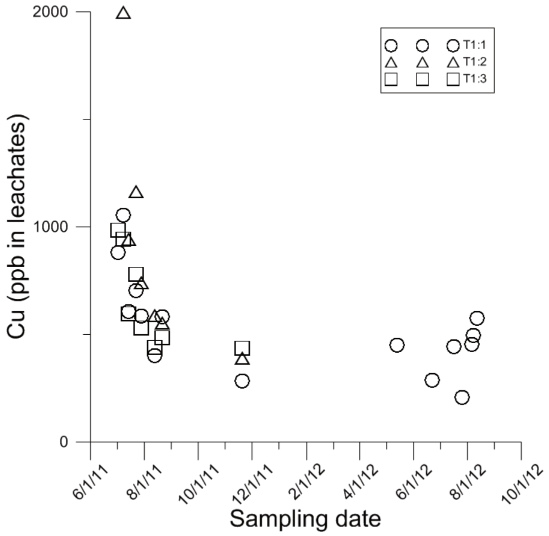

Fig. 1 *Cu-concentration in leachates from T1 during the first and second growth season.*

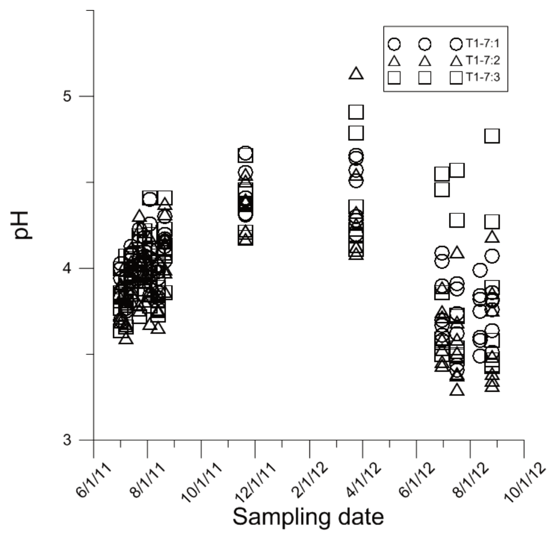

Fig. 2 *Variation of pH in leachates from T1 to T7 during the first and second growth season.*

higher initial release of Cu but the total removal was highest for those two treatments over two seasons (table 2).

During the first season pH increased with 0.5 to 1 unit in all systems. Initially a minimum of approximately 3.5 was observed which increased to a maximum of approximately 4.5 (Fig. 2). Apparently this was related to the high release of humic substances (Karlsson *et al.* 2013) from the bark compost and their collective buffering capacity. As the concentrations of DOC went down during the second season there was an increased variation of the pH for all treatments (Fig. 2). There was also a general decrease in pH with final readings close to or below their initial values. At this point, the readily available humic substances had been leached from the substrate and the DOC concentrations were lowered to some 10 mg L^{-1} of non-humic carbon compounds (Karlsson *et al.* 2013). Hence, the increase in pH during the first season might also have been influenced by heterotrophic production of alkalinity by the microbial community.

A clear decreasing trend in the electrical conductivity was found during the first season in all treatments, from approximately 2 – 0.8 mS cm^{-1}. The concentrations of Cu followed the development of electrical conductivity (r^2 0.82), although this ion is not a dominating constituent. As the electrical conductivity increased to some 1.5 mS cm^{-1} by the end of the second season its correlation with Cu became weaker (r^2 0.61). Hence, it appears as if different mechanisms controlled the concentrations of dissolved Cu. Equilibrium modeling indicated three major (> 5 %) Cu-species in the solution phase. Both initially and after two seasons Cu^{2+} accounted for some 75 %. Aqueous Cu-sulfate and Cu bound to organic carbon made up the remaining 25 %. The initial distribution was approximately 15 % and 10 % of Cu-sulfate and Cu bound to organic carbon, respectively, while the final distribution had changed to approximately 5 % and 20 %. The calculated saturation indices for predicted Cu-minerals were all below -5 why it is unlikely that any precipitation of stoichiometric Cu-phases occurred. Co-precipitation with Fe was also an unlikely redistribution mechanism since the only predicted mineral was cupric ferrite which had a saturation index below -13. The increase of organic Cu-complexes in solution suggests that a similar mechanism might explain the increased sorption of Cu. Hence, it can be concluded that the immobilization of Cu-ions at low pH, was caused by adsorption either directly to the surface of the bark compost or by adsorption of the Cu-organic complexes. It is not clear if the organic ligands originate from a physical release from the bark compost or if they were excreted from the microbial community.

Conclusions

By adding bark compost, WWG and living mycorrhiza to weathered sulfidic mine waste the growth of A. capillaris was promoted. Probably three factors were involved: i) adsorption of Cu to the bark compost or macromolecules from the same, ii) adsorption of Cu to macromolecules released from the mycorrhiza, and iii) neutralization of generated acid in the root zone. Hence, the growth was promoted due to detoxification of the pore water.

By adding bark compost to the sulfidic mine waste up to 80 % of the available phytotoxic Cu was retained in the solid phase. In combination with the surface stabilizing effect of A. capillaris it seems like addition of bark compost and A. capillaris can be a successful first action to minimize the environmental impact of phytotoxic Cu from sulfidic mine waste. However, it may be necessary to combine it with other additives such as mycorrhiza and alkaline material to promote the growth of A. capillaris. Before performing large scale operations the adsorption of Cu to bark compost or immobilization by root exudates must be better understood, in order to avoid secondary release of immobilized Cu-species in a longer time frame than in these experiments.

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