Revegetation of historic acidic mine waste with *Agrostis capillaris* – Impact on leachate composition in pot experiments

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Abstract

Pot experiments have shown that the grass *Agrostis capillaris* can be established on historic acidic mine waste from Ljusnarsberg in Sweden. The addition of bark compost was evaluated in combination with different alkaline industrial waste products as well as mycorrhiza. The best result was found for the combination of water works granules and mycorrhiza. During the growth season the percolation water from the pots showed qualitative changes as a response to the amendments; increased pH and lowered concentrations of most elements, except for calcium and lead. At the end of the growth season most environmentally critical elements had solution concentrations below those of untreated systems.

Keywords: historic acidic mine waste, *Agrostis capillaris*, alkaline refuse, bark compost, mycorrhiza

Introduction

Establishing a vegetation cover is often used either as a final step or as the only treatment in the remediation of contaminated soil or dump sites (c.f. Nathanail and Bardos 2004). It is seldom used as the only action taken to protect the environment from metal contamination from historic acidic mine waste. The reasons are simple; often the mine waste is too coarse to store water for plants, acidity has a negative impact as well as high concentrations of toxic metals. In addition, these sites are usually very poor in nutrients. The proportion between these negative factors varies between different sites as a function of mineralogy, but it is usually one or several of them that make re-vegetation impossible.

In a recent pot study it was demonstrated that the grass *Agrostis capillaris* might be a suitable species to re-vegetate acidic mine waste (Karlsson *et al.* 2012). In its original state the acidic mine waste was inhabitable for all species that were tested, which is understandable since no vegetation cover exists on the heaps. Although the acidic mine waste gave a pore water pH around 3 and released high concentrations of metals the addition of bark compost, water works granules and mycorrhiza gave a positive result. These additives served to improve the water holding capacity, increase the pH in the root zone and facilitate nutrient uptake. Several other additives were evaluated in the study and it was noticed that the composition of the drainage water changed in a systematic way during the growth season. In general, there was an increase in pH and lowered concentrations of dissolved metals from the acidic mine waste, with the exception for calcium and lead (Karlsson *et al*. 2012).

Here, we report on the systematic changes when the top 50 mm of a mixture with acid mine waste (70%) and bark compost (30%) received small additions of water works granules (wwg), mycorrhiza and Aspen (*Populus tremula*) shavings in different combinations.

Methods

Sieved (< 5 mm) acidic mine waste from the Ljusnarberg deposit in Sweden was used as model material. The waste is a complex mixture of carbonate (Ca, Mg) and sulphide (chalcopyrite, galena, pyrite, sphaelerite) minerals in a matrix of pegmatite, granite and aplite as well as skarn minerals. Also biotite, phlogopite and muscovite are commonly found as well as fluorite, and related fluoride minerals (c.f. Sartz 2010). The waste was mixed with bark compost (commercial from Bauhaus) to 30%. The refuse presented here is water works granules (wwg) which is a waste product from softening of drinking water with a technology used by many Swedish public water works. It consists of Ca/Mg carbonate and traces of elements that adsorb to this matrix. The third additive was mycorrhiza that had been isolated from the site was added either living or dead, as reference. The final additive consisted of Aspen (*Populus tremula*) wood shavings. After three weeks two of the pots received a single dose of a commercial inorganic fertilizer.

Ordinary flower pots (180 mm outer diameter. x 160 mm height) were used and each treatment was done in triplicate. The substrate was prepared by thoroughly mixing the mine waste and the bark compost. The additives were then mixed into the top 5 cm except for the wood shavings that were mixed into the whole volume. The combination of additives is given in table 1. The pots were then put on a corrugated and painted metal slate in the garden at Listregården (50°22´28.95´´N 15°17´37.43´´E).

***Table 1** Composition of the test series.*

Test series	Bark compost (%)	wwg	Mycorrhiza dead	Mycorrhiza living	Aspen wood shavings
1	30%				
2	30%	Yes			
3	30%		Yes		
4	30%			Yes	
5	30%	Yes	Yes		
6	30%	Yes		Yes	
7	30%				Yes

The weather conditions (temperature, rain volumes, humidity, wind direction and speed) were recorded every fifteen minutes. Samples of the percolation water from the pots were taken once a week during the eight weeks of the experiment by watering the pot with 10 mm of rain water. One additional sampling was made in November, just before freezing. The samples were frozen immediately after sampling and remained frozen until they were analysed.

The samples were measured for electrical conductivity (EC) and pH with conventional electrodes. Principal anions (F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_3^{2-}, HSO_3^-, SO_4^{2-}) were quantified with ion chromatography. Dissolved organic carbon (DOC) and inorganic carbon (IC) were quantified with a Shimadzu TOC-V CPH instrument. These samples were filtered through a 0.20 µm polycarbonate filter. They were also used to prepare the dissolved fraction of metals (Li, (Ba), Be, Na, Mg, Al, K, Ca, V, Cr, Fe, Mn, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Mo, Ag, Cd, Ba, Tl, Pb, Bi and U). Quantification of metals was made with ICP-MS (Agilent 7500cx). The reaction cell was operated in collision mode (helium) for measurements of As, Ca, Fe, Se and V. The statistical analysis with Pearson correlation and two way ANOVA analysis was made with the Systat software (Systat Software Inc.). The geochemistry was evaluated by the use of Visual MINTEQ.

Results and Discussion

Weather conditions

The sowing took place in mid June when the rather cold spring had turned into slightly warmer conditions. After a few weeks with dry and sunny weather it turned into rather humid conditions with almost daily showers of a few mm. This resulted in an accumulated liquid to solid ratio (L/S) around 5 (figure 1) by the end of the experiment after 8 weeks. The weather conditions are summarised in Karlsson *et al* (2012).

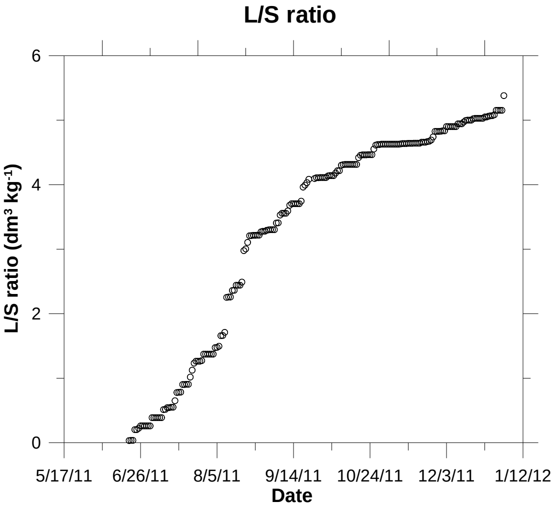

Figure 1 *Accumulated liquid to solid ratio (L/S) during the time of the experiment.*

The evaluation of the growth in the different systems is presented elsewhere (Karlsson *et al*. 2012) but a short summary is given here for the readers' convenience. The longest shoots were found in series 2 (wwg), 6 (wwg and living mycorrhiza) and 7 (wood shavings and fertilizer). Since the most likely amendments under field conditions would be those in series 2 and 3 they are discussed in more detail in the following paragraphs.

Table 2 *Average composition (n = 3) of the percolation water in series 1 (reference), 2 (wwg) and 6 (wwg and living mycorrhiza) at three occasions during the experiment and the three year averages for field leaching experiments according to Sartz (2010).*

	Series 1			**Series 2**			**Series 6**			**Sartz 2010)**
Week	**1**	**7**	**8**	**1**	**7**	**8**	**1**	**7**	**8**	
EC (mS/cm)	1.579	1.129	0.841	1.489	1.078	0.796	1.592	1.004	0.746	2.838
pH	3.88	4.03	4.24	3.86	4.15	4.43	3.90	4.24	4.51	3.15
SO_4^{2-} (mg/L)	704	1282	562	1535	1137	598	817	1027	644	1890
F^- (mg/L)	41.9	31.9	17.6	95.5	28.3	13.6	39.1	19.2	13.7	n.d.
Cl^- (mg/L)	4.39	0.60	1.09	9.32	0.54	1.00	3.58	0.48	1.2	n.d.
DOC (mg/L)	41.5	15.3	9.0	49.0	13.3	10.0	44.7	10.2	9.4	n.d.
Al (mg/L)	21.9	13.5	9.9	20.1	13.6	8.4	19.0	8.4	7.1	20
Ca (mg/L)	85.8	291.4	214.0	145.9	245.4	208.8	94.3	261.2	197.2	209
Fe (mg/L)	0.41	0.21	0.13	0.57	0.19	0.12	0.33	0.17	0.12	132
K (mg/L)	24.7	9.1	3.7	29.0	8.1	4.3	27.9	5.7	3.8	9.2
Mg (mg/L)	48.7	9.4	2.4	55.3	9.1	3.4	49.5	6.5	2.3	51.6
Mn (mg/L)	29.6	8.5	1.2	34.2	7.2	1.7	29.8	4.2	1.0	4.2
Na (mg/L)	5.7	1.5	1.3	7.2	1.8	1.4	5.9	1.1	1.4	7.8
As (µg/L)	0.22	0.14	0.03	0.25	0.04	0.06	0.24	0.08	0.05	n.d.
Cd (µg/L)	129	90	44	162	71	39	129	49.8	31.1	128
Co (µg/L)	99.6	43.2	11.9	114.6	33.0	13.3	31.6	20.9	8.9	n.d.
Cr (µg/L)	0.53	0.51	0.80	0.70	0.26	0.83	0.64	0.29	0.66	n.d.
Cu (µg/L)	933	541	371	1321	467	330	823	300	248	n.d.
Ga (µg/L)	2.28	2.92	2.43	2.78	2.53	2.57	2.52	3.05	2.27	n.d.
Ni (µg/L)	42.1	21.8	11.7	38.9	17.3	10.7	31.6	12.5	8.9	n.d.
Pb (µg/L)	34.6	185.2	118.7	58.3	154.5	93.1	24.3	121.5	72.6	2200
Sr (µg/L)	170.7	309.7	126.4	294.4	281.4	156.1	192.8	250.3	134.4	176
Tl (µg/L)	0.92	1.51	0.79	1.23	1.29	0.65	0.86	1.03	0.52	n.d.
U (µg/L)	0.61	0.12	0.06	0.29	0.09	0.04	0.21	0.04	0.03	n.d.
Zn (µg/L)	48107	25610	10219	57722	19262	9969	48022	12983	7480	17000

n.d. not determined

General hydrochemistry

During the time of growth the concentrations of dissolved ions in all systems had a similar tendency towards lower values, as illustrated by electrical conductivity (figure 2). Initially, the electrical conductivity was within the range presented by Sartz (2010) for a three year field leaching study (table 2) but at the end they were significantly lower. Hence, all strategies that were evaluated seem to improve the environmental conditions, including the reference with bark compost. All principal cat- and anions followed this pattern, except for sulphate that had fairly constant concentrations and calcium whose concentrations increased with time.

The pH had increasing tendencies in all series (table 2), from 3.9 to 4.5, in comparison with 3.15 reported by Sartz (2010). The mechanism behind the increase is not elucidated in detail but it is highly likely that there was a contribution from the DOC that was released from the bark compost. This rather modest increase would, however, have a limited impact on plant growth as well as metal mobility.

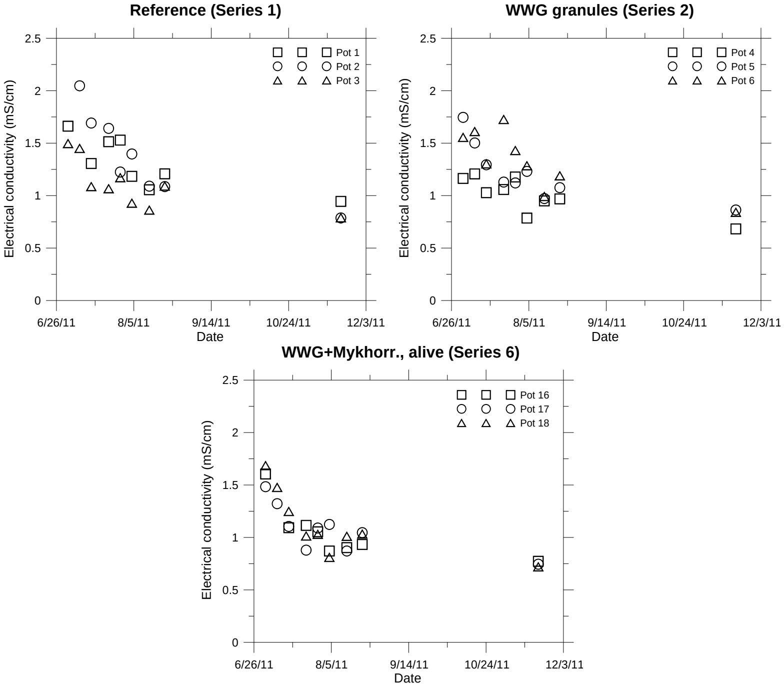

Figure 2 *Electrical conductivity (mS cm*$^{-1}$*) as a function of time.*

The release of DOC from the bark compost was the major difference when compared to the field leaching experiments (figure 3). During the experiment there was a pronounced lowering of DOC (table 2) and it followed the patterns for electrical conductivity, just as the principal ions. A high correlation ($r > 0.80$) was found between DOC and the majority of the dissolved metals. Hence, addition of the bark compost released a mobile organic fraction that seemed to reach some kind of equilibrium, or steady state, by the end of the experiment. Any contribution of metals from the bark compost was negligible in relation to the mine waste so it is highly unlikely that it should have contributed to the dissolved metal concentrations. The molecular weight distribution of the DOC and its fluorescence properties resembled those typical for fulvic acids (not illustrated). Applying a NICA-Donnan model for the stability of metal fulvate complexes with properties for an “average” fulvic acid indicated a high impact on the speciation of dissolved metals. Therefore, the addition of the bark compost produced a fraction of high molecular weight metal complexes.

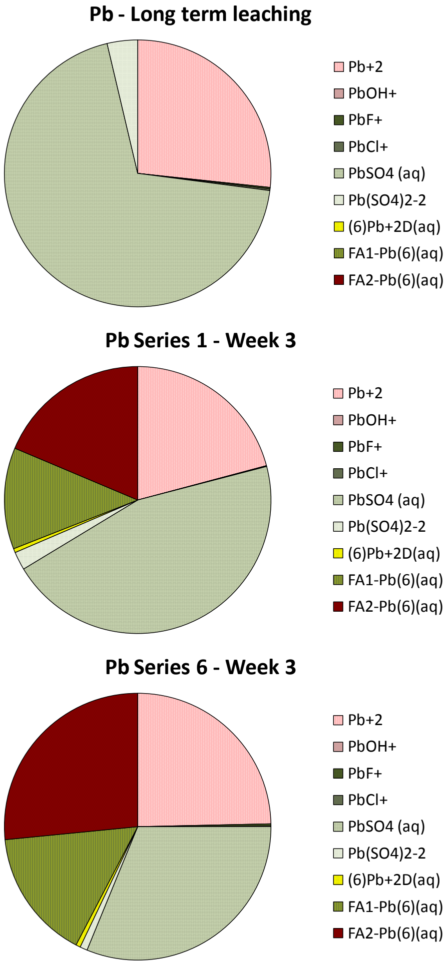

Figure 3 *Distribution of dissolved lead species.*

The high correlation between dissolved metals and DOC infers that the bark compost increased the mobility of the metals in the system, at least initially. Although the metal concentrations were lower at the end of the pot experiment than in the long term field experiment it is unclear if this is related to only the addition of the bark compost, the other additives or to the growth of the plants.

Saturation and speciation

The aqueous phase in the long term leaching experiment was in equilibrium with or slightly oversaturated with respect to anglesite, anhydrite, barite, chalcedony, cristobalite, fluorite, gypsum and quartz. Aluminium did not reach solubility limiting concentrations and only $AlOHSO_4(s)$ went towards equilibrium but the saturation index was only -3.0. The iron system was undersaturated and the dissolved species were dominated by the divalent state, where the sulphate complex accounted for more than 50% of the iron species in solution.

The solubility limiting phases in series 1 (mine waste and bark compost) at week 3 and 8 were essentially the same as in the long term leaching experiment, but with some exceptions. The qualitative impact of the DOC is evident and particularly important for metals that either form stable complexes with humic substances or is present at high concentrations. For instance, anglesite was not a solubility limiting phase in the pot experiments, since a higher fraction of dissolved lead had formed complexes with the DOC. The same applies to fluorite since enough calcium ions had formed DOC complexes to leave fluorite undersaturated. This was of particular importance since it also left a higher fraction of fluoride ions available for formation of complexes with aluminium ions. The impact of the amendments was identical for series 6 (wwg and living mycorrhiza), in spite of improved plant growth, and solubility limiting concentrations were reached for the same set of minerals as in series 1. Thus, the DOC concentrations in the pot experiments were high enough to maintain several metal species in solution, even at the end of the experiment when the DOC concentrations were some 10 mg/L. This corresponds to a fulvic acid concentration of approximately 5 mg/l which is commonly found even in soils with low biological production. Under these conditions redistribution processes for the trace metals would to a higher extend be controlled by adsorption processes, than in the field leaching experiment.

Indicators on weathering

The strong relationship between electrical conductivity and metal concentration did not apply to gallium and strontium since they had similar concentrations throughout the study, independent of treatment. These elements would represent the behaviour of the parent rock assembly rather than the sulphides so the results imply that the weathering rate of this material was essentially constant. A similar reasoning applies to the sulphide phases since the sulphate concentrations also were fairly constant in all treatments (table 2). It should be remembered that the time period was only eight weeks. Thus, in spite of limited impact on the weathering rates the concentrations decreased for the majority of elements in the aqueous phase.

Impact of biota

The results from the correlation analysis suggest that there was a limited impact of biota on metal mobility. Instead, the differences between the pots in the experiment and the long term leaching might be controlled by the bark compost. An attempt to reveal the relationship between growth and chemical composition of the effluent was made by using an ANOVA test. In this analysis the variance of the residuals from a regression model was examined, where the tested variable was set as dependent while time (sampling occasion) and additive (series) were the independent variables. In this way, any relationships between changing metal concentrations, kind of additive and time should be revealed. Particular attention is paid to the impact of DOC since the correlation analysis revealed a strong relationship between the concentrations of most ions and DOC.

This analysis showed (figure 4) that there were no differences ($p < 0.05$) in the concentrations of DOC that could be attributed to the different additives and combinations, with one exception. In series 7 (Aspen wood shavings) the initial concentrations of DOC were higher than in any of the other treatments. This observation is perhaps not so surprising since the material is an additional source for nutrients. As time progressed any differences levelled out and the concentrations of DOC were lowered in a similar fashion independent of additive. This is another strong indication that the DOC had a large impact on the systems. Production of DOC from biota could not be detected in these systems because of the dominating contribution from the bark compost.

Similar results were found for the concentrations of dissolved metals, i.e. no significant systematic differences were detected as a function of additive and time. Just as for DOC a slight hysteresis was found during the first weeks but then the in series differences are levelled out. Although not significant ($p < 0.05$) there was a tendency for lower concentrations of dissolved metals (notably cadmium, copper, iron, lead and zinc) in series 6 (wwg and living mycorrhiza) than in the other systems. This system had the second highest grass production why some of these elements might have been taken up in the biomass or immobilised in the substrate due to chemical changes in the microenvironment.

Conclusions

This study has demonstrated that the combinations of amendments that provided the best growth conditions for *Agrostis capillaris* (i.e. bark compost with water works granules and mycorrhiza) also gave the lowest concentrations of dissolved metals. The relative impact from the bark compost, water works granules and mycorrhiza cannot be separated with the available data at a reasonable probability level ($p < 0.05$). The circumstances strongly indicate that the major impact is attributable to the bark compost but the mechanisms remain to be elucidated.

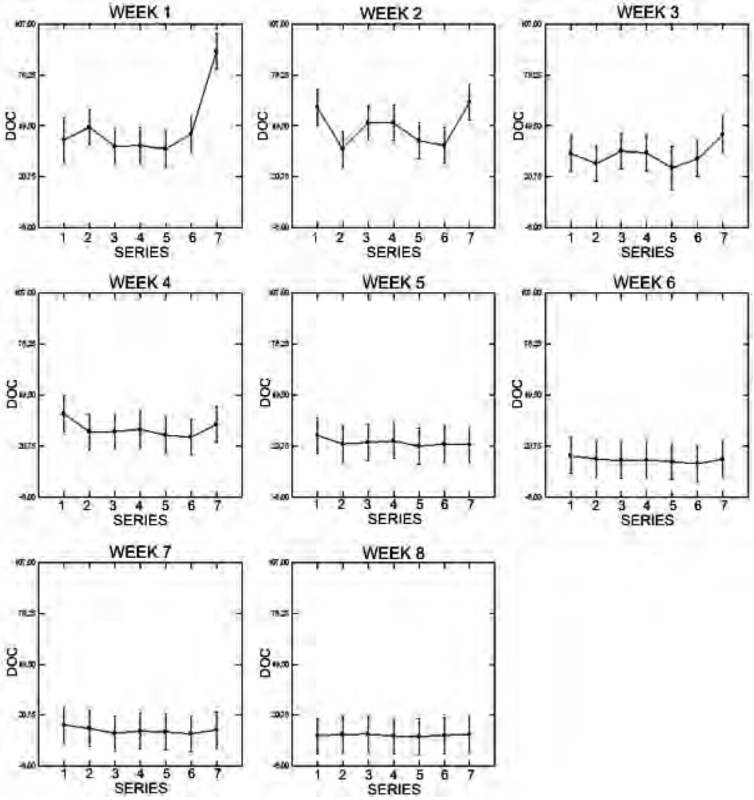

***Figure 4** Anova analysis of the concentration of DOC as a function of amendment (SERIES) for sampling occasions week 1 to 8.*

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