

Leaching pattern of metals from historic sulphidic mine waste upon addition of bark compost

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Abstract The drainage water from pot experiments where *Agrostis capillaris* was grown on a mixture of 70 % (volume) sulphidic mine waste and 30 % (volume) bark compost was monitored for general hydrochemical parameters, dissolved metals and organic carbon during two years. During the first months there was a significant release of DOC from the bark compost that decreased from 80 mg L⁻¹ to 10 mg L⁻¹ at week 1 and 14, respectively. During the second year the DOC remained at some 10 mg L⁻¹. In the early stage the DOC consisted of molecules in both the fulvic acid size range (80 % of DOC concentration) and that of humic acids (20 % of DOC concentration). The quantitative impact of the humic substances was indicated by correlation coefficients larger than 0.9 with several metals (Al, Cd, Cu, Fe, K, Mg, Mn, Na, Ni and Zn) and principal anions (Cl⁻ and F⁻). For SO₄²⁻, Ca and Pb there was no or weak correlation with DOC and their concentrations increased with time. The change in pH from 3.7 to 4.2 during the time of the study would have had a limited impact on the stability of any metal humic complexes. Hence the lowered metal mobility is attributed to adsorption of the metal-fulvate complexes. These results illustrate that addition of bark compost and its leachable humic substances influence the mobility of metals from the sulphidic mine waste but not always in a theoretically predictable manner. Hence, the properties of an organic additive should be determined experimentally before use.

Keywords Historic sulphidic mine waste, grass cover, solution chemistry

Introduction

In Sweden historic sulphidic mine waste is a common problem because of a mining history that began almost some 1000 years ago, although the highest amount was produced after circa 1700. Although "historic" is a relative term it usually refers to waste that was produced before the Second World War. The typical site is small (some ha), with a high metal content (usually %) and acid generating potential and it is found far from modern infrastructure such as roads and electricity (SEPA 2013). This combination makes it very costly to use the standard procedures with either dry or wet covers why other strategies are required. Among these, the establishing of vegetation covers is probably a good alternative since it would stabilize the surface from erosion and

reduce infiltration of rain water (Ahn *et al.* 2011; Nathanail and Bardos 2004). With this approach it is difficult to fully prevent the production of leachate so it is probably necessary to include some kind of passive water treatment system with long term sustainability. However, just reducing the production of contaminated water might be sufficient on many sites.

In boreal environments the impact of local climate must be added to the more common challenges such as low water holding capacity and limited access to nutrients in the waste. In central Sweden, where the majority of small waste piles are found, the soil is frozen from mid-November until early May. In addition, in late autumn and early spring there are several weeks with daily cycles of freezing and

thawing which adds another stress factor to vegetation. Also summer poses some serious threats. The waste sites are usually free from all kind of vegetation why temperatures around 60-70 °C are reached at solar noon on a typical summer's day. At night it is not too uncommon to find frost, at least until the end of June. Finally, the toxic properties of the waste must be considered.

In this harsh environment we are evaluating how the UMBRELLA concept (UMBRELLA 2013) performs when establishing a grass cover with *Agrostis capillaris var. metallica* and if growth can be sustained over several seasons. In brief, this strategy uses an optimized assembly of microorganisms to supply the plants with nutrients. No fertilizers or biocides are used why a minimum of maintenance is required. In principle, this approach is also suitable for phyto-extraction and stabilization. Because of the poor conditions for growth in the material from the Ljusnarsberg mine waste site (Sartz 2010) that served as the substrate in this study we evaluated the impact of increased water holding capacity by mixing it with compost and addition of carbonaceous refuse in the root zone. During the first growth season in 2011 the plants survived although the growth was quite limited (Karlsson *et al.* 2012a, b). The best growth was found in a treatment with water works granules combined with mycorrhiza. Concentrations of dissolved organic carbon and all metals studied, except calcium and lead, decreased with up to one order of magnitude. Here we report on the composition of the solution phase with focus on organic constituents and metal concentra-

tions as a function of treatment during the first two years of the experiment.

Methods

The methodology that was used in this study has been described elsewhere (Karlsson *et al.* 2012b) but a summary is given here for the readers' convenience. Sieved (< 5 mm) mine waste from the Ljusnarsberg mine site, Sweden, was mixed with commercially available bark compost by 30 % (volume) to improve its water holding capacity. After homogenization the mixture was put in ordinary plastic flower pots. Each pot contained some 1.8 L of the substrate and all amendments were mixed into the top 5 cm, according to table 1. The amendments consisted of i) mycorrhiza for improved nutrient availability; ii) water works granules (wwg; Ca/Mg carbonate from water softening) to increase pH in the root zone and iii) Aspen (*Populus tremula*) shavings to support the heterotrophic community of microorganisms. The pots were sown with *Agrostis capillaris* and put outdoor. Water was administered weekly (10 mm) during dry periods. Sampling of the drain water was made after rain falls or watering. The samples were frozen immediately.

The analytical protocol included electrical conductivity, pH, principal anions (Ion chromatography) and metals (ICP-MS; Agilent 7500 cx). Dissolved organic constituents were analyzed as: i) Total organic carbon (TOC) with a Shimadzu TOC-V CPH instrument; ii) Molecular weight distribution by size exclusion chromatography (Toso Haas TSKgel 2000 SW and Agilent SEC-5 columns) and iii) as low molecu-

Treatment	Function	Material
1	Reference	No additions
2	Increase pH	Water works granules (wwg)
3	Nutrient availability (reference)	Mycorrhiza ^a , dead
4	Nutrient availability	Mycorrhiza ^a
5	Nutrient availability and pH (reference)	Mycorrhiza ^a (dead) and wwg
6	Nutrient availability and pH	Mycorrhiza ^a and wwg
7	Easily accessible carbon	Aspen (<i>Populus tremula</i>) shavings

^a Kindly provided by Prof K Turnau, Jagiellonian University, Krakow, Poland

Table 1 Additives in the pot experiments.

	El Cond. mS cm ⁻¹	pH	F ⁻ mg L ⁻¹	Cl ⁻ mg L ⁻¹	SO ₄ ²⁻ mg L ⁻¹	Na mg L ⁻¹	Mg mg L ⁻¹	Al mg L ⁻¹
Mine waste	2.40	3.22	98.0		2275	1.18	95.6	59.6
Compost	0.57	7.20		113	21	29.3	12.2	0.40
	K mg L ⁻¹	Ca mg L ⁻¹	Mn mg L ⁻¹	Fe mg L ⁻¹	Cu mg L ⁻¹	Zn mg L ⁻¹	Cd µg L ⁻¹	Pb mg L ⁻¹
Mine waste	1.2	547	11.9	3.72	8.92	133	391	1.20
Compost	96.4	59.4	0.10	0.05	0.09	0.06	0.30	0.02

Table 2 General composition of water extracts (L/S 10) of mine waste and bark compost.

lar weight carboxylic acids (Dahlén *et al.* 2000). All chromatograms and interpherograms were evaluated manually.

Results and discussion

The composition of the leachate water from the waste has previously been determined in long term leaching systems on the field site (Sartz 2010) as well as in several short term leaching with water at a liquid to solid ratio (L/S) of 10 (table 2).

It is evident that the two materials released different concentrations of all ions and that the compost buffered pH at near neutral. The concentrations of DOC in the leachate from the compost had a concentration around 100 mg L⁻¹ whereas those from the mine waste were below detection, *i.e.* lower than 0.05 mg L⁻¹. From the long term leaching experiments on the field site DOC concentrations varied from below the limit of detection to some 1 mg L⁻¹. The origin of this DOC is uncertain but high microbial weathering activity might release organic carbon. However, it is fair to conclude that the pot systems discussed here are influenced by the compost not only concerning the water holding capacity but also from qualitative features of the released DOC.

The quality of the DOC in the water leaching experiment, according to the SEC analysis, was dominated by two size classes. Average molecular weight estimates, UV/Vis spectra and SUVA index as well as their fluorescence spectra indicate the presence of humic and fulvic acids. Since these estimators are not definitive, the presence of *e.g.* peptides and proteins in these size ranges is possible. The absolute

concentrations of the two humic substances were not determined since it involves a rather extensive procedure for cleanup but their absorbance properties indicate a ratio of 20 % and 80 % of humic and fulvic compounds, respectively.

The compost also released low molecular weight organic compounds (LMWOC) in the water leaching but at a rather low DOC concentrations, seldom more than 1 mg L⁻¹. Screening with CE showed that this fraction was dominated by acetic acid, possibly indicating that the compost had been stored in plastic bags until it was bought.

Both the compost itself and the released DOC had a large impact on metal distribution (Karlsson *et al.* 2013; Sjöberg *et al.* 2013) by adsorption to the solid matter as well as complexation in the solution phase. Hence, the qualitative impact in the pot experiments can be expected to influence not only adsorption controlled metal distribution but also solubility equilibria.

In the pot experiments all systems behaved in a similar way and there was a high release of ions during the first weeks, as illustrated by the electrical conductivity (Fig. 1). During the following weeks the ion content of the solution phases were approximately halved, and then returned to their initial levels during the second summer. The large decrease in July 2012 illustrates the impact of heavy rain events, resulting in a temporary dilution.

DOC behaved in a different manner and no increase was found during the second summer (Fig. 1). Instead the concentrations remained at some 10 mg L⁻¹, just as at the end of

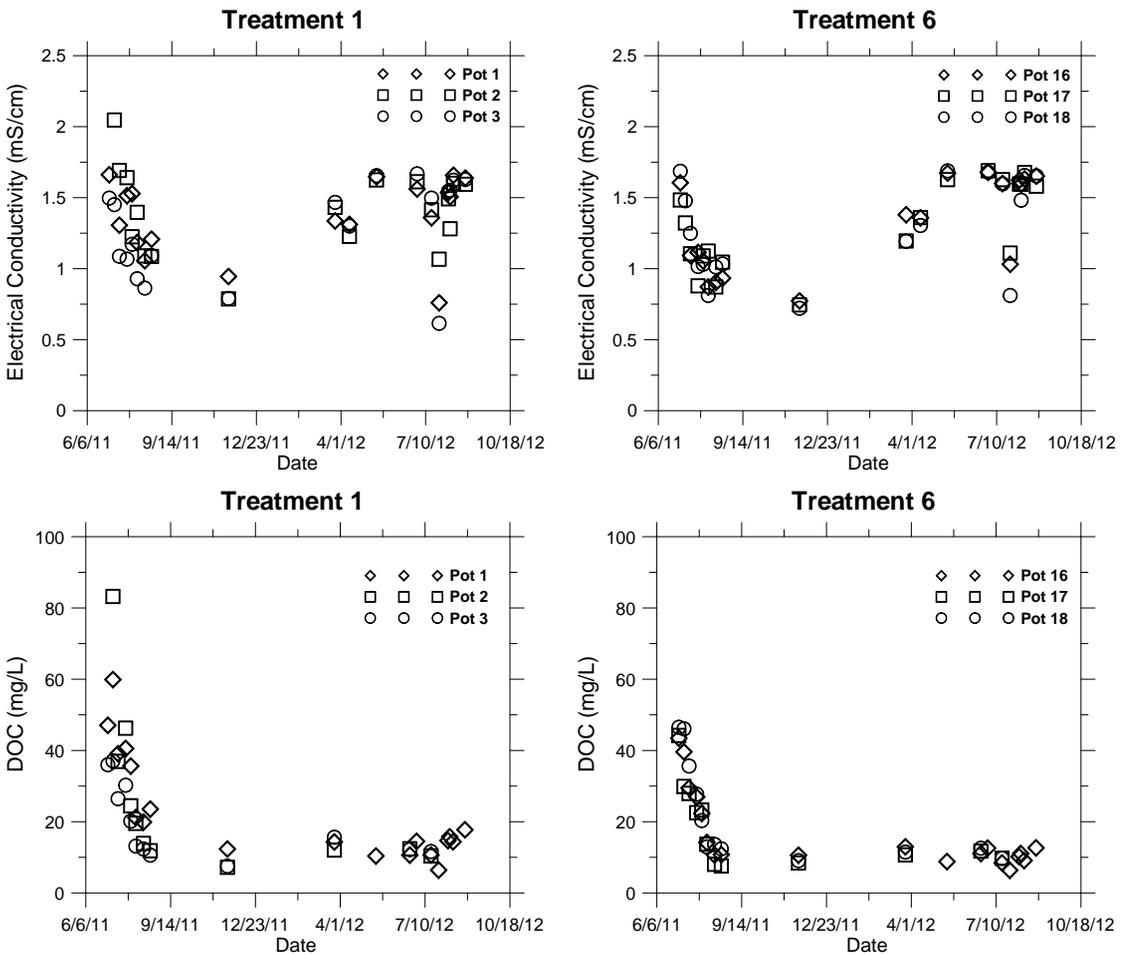


Fig. 1 Electrical conductivity ($mS\ cm^{-1}$) and DOC ($mg\ L^{-1}$) as a function of time in treatments 1 and 6.

the first summer. The reasons are not clear in detail but it is likely that heterotrophic microbial activity released the DOC at this steady state concentrations. The quality of the DOC has also changed and no humic acid sized compounds could be detected. Instead the LMWOC fraction increased up to some $5\ mg\ L^{-1}\ C$ and contained several carboxylic acids indicative of heterotrophic activity.

In many acidic mine waters there is a high correlation between electrical conductivity and element concentrations in the dissolved phase and so is the case for the long term leaching experiments of this mine waste (Sartz 2010). In the pot experiments, however, a different pattern of correlations emerged (Table 3). The correlation coefficients between the

dissolved metal concentrations and the electrical conductivity are essentially lower than those for DOC. This pattern was also found for the dominating mineral forming elements such as aluminum and iron. Calcium and lead behaved differently and their concentrations followed more the development of electrical conductivity. These results illustrate that the electrical conductivity is a poor estimator for the concentrations of dissolved metals when sulphidic mine waste is mixed with bark compost.

Among the most toxic elements discussed here lowered concentrations were found for Cu, Zn and Cd but also Ni behaved in a similar way, contrary to the development of electrical conductivity. The concentrations of

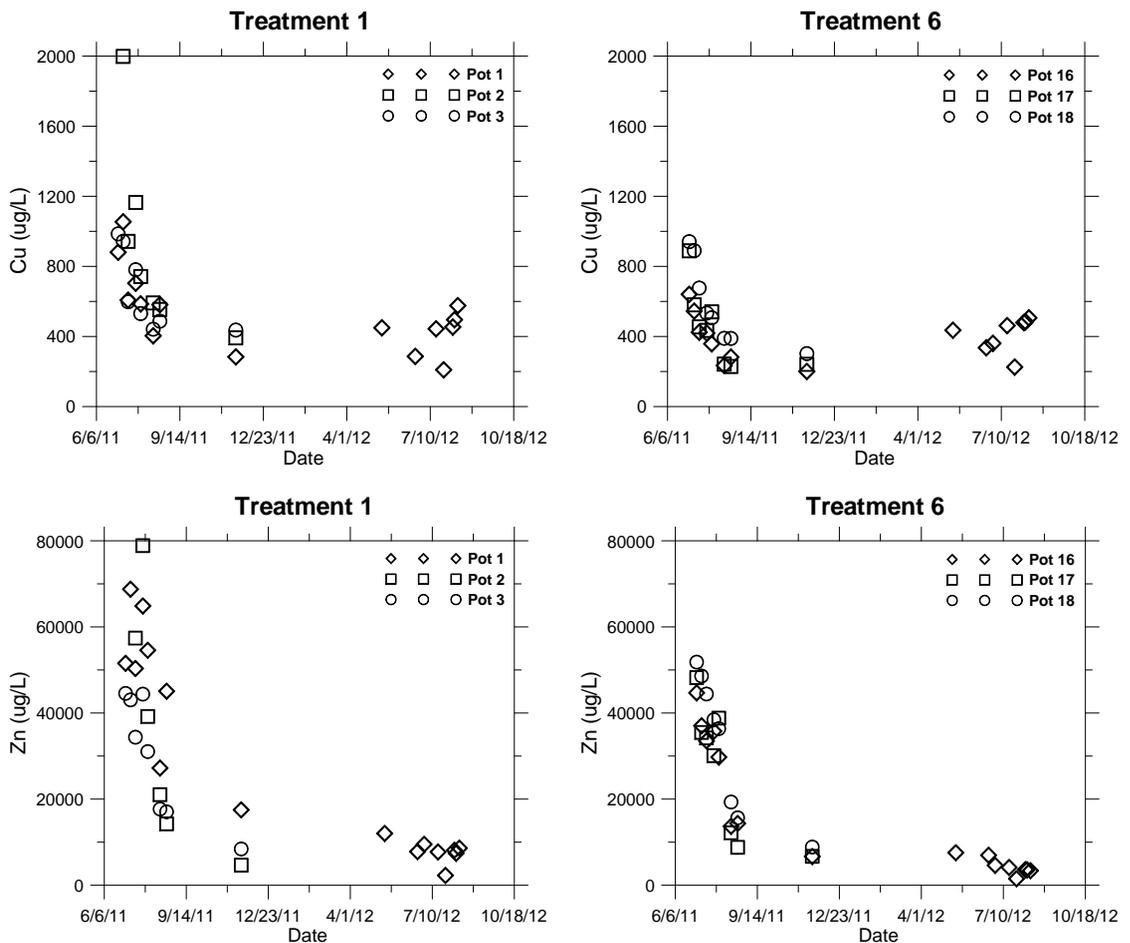


Fig. 2 Concentrations ($\mu\text{g L}^{-1}$) of copper and zinc as a function of time in treatments 1 and 6.

uranium were lowered but its relationship to DOC was less evident than for the previous elements. Geological modeling indicated under-

saturation of all transition elements and aluminum whereas the concentrations of Pb were influenced by formation of anglesite. The

	El.cond.	DOC	Na	Mg	Al	K	Ca	Fe	Mn	Cu	Zn	Cd
El.cond.	1											
DOC	0.52	1										
Na	0.49	0.92	1									
Mg	0.55	0.98	0.95	1								
Al	0.64	0.90	0.86	0.90	1							
K	0.60	0.95	0.95	0.96	0.89	1						
Ca	-0.37	-0.38	-0.42	-0.39	-0.21	-0.033	1					
Fe	0.77	0.85	0.71	0.82	0.80	0.74	-0.36	1				
Mn	0.51	0.97	0.96	0.99	0.90	0.96	-0.36	0.80	1			
Cu	0.78	0.86	0.77	0.87	0.92	0.80	-0.22	0.90	0.87	1		
Zn	0.84	0.95	0.92	0.98	0.96	0.95	-0.28	0.78	0.98	0.89	1	
Cd	0.52	0.93	0.92	0.95	0.94	0.92	-0.20	0.76	0.97	0.90	0.99	1
Pb	0.26	-0.40	-0.44	-0.44	0.23	-0.33	0.81	-0.27	-0.47	-0.10	-0.18	-0.42

Table 3 Correlation coefficients for some quality parameters for all treatments in leachates 2011- 2012.

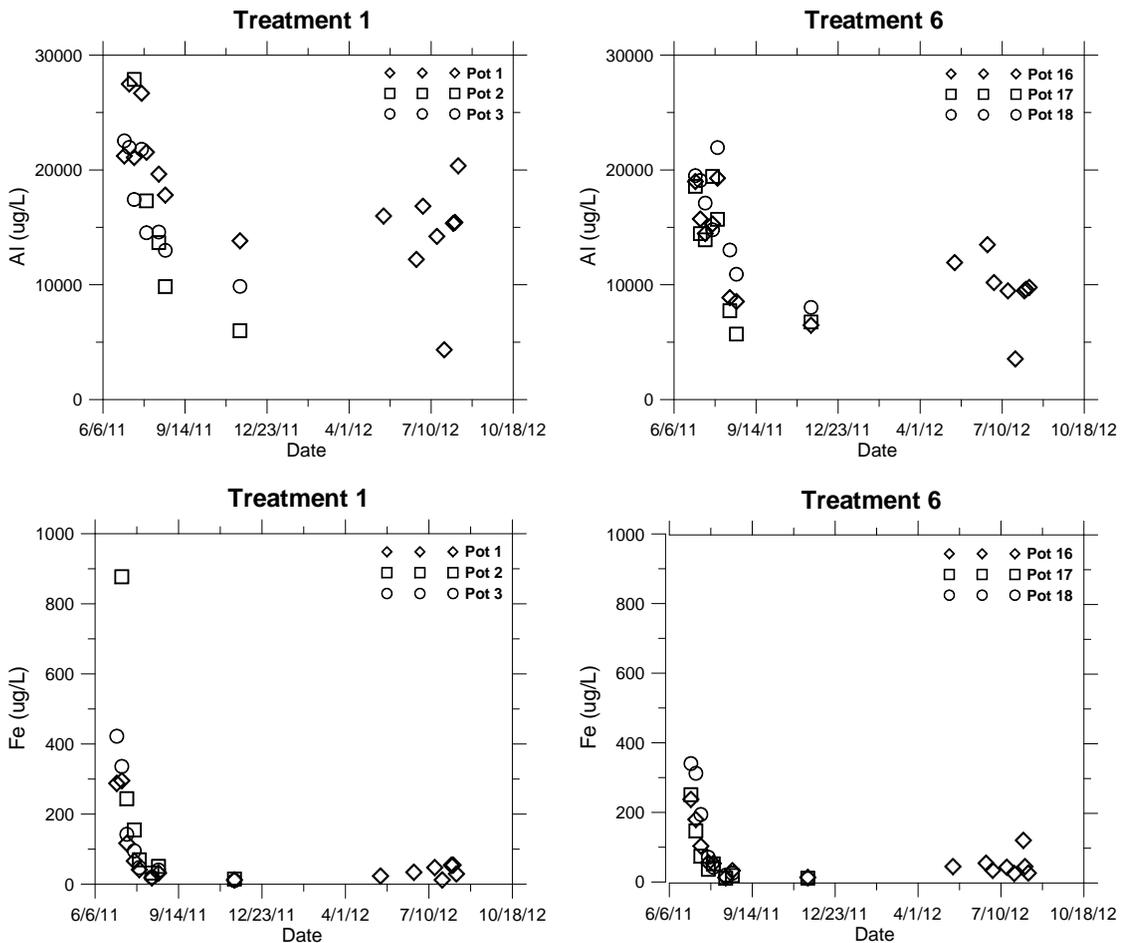


Fig. 3 Concentrations ($\mu\text{g L}^{-1}$) of aluminum and iron as a function of time in treatments 1 and 6.

modeling also indicated a high impact of their respective fulvate complexes. Assuming that the humic substances have an average carbon content of 50 % and a cation-exchange capacity of 10 meq g^{-1} they accounted for a complexing capacity in the range of 5 – 50 meq L^{-1} . Such complexes have a highly different pH dependent adsorption. In general, adsorption is increased in the low pH range but lowered in the high pH range. Hence, under the solution conditions in this study there are reasons to assume a lower mobility of these complexes through adsorption.

At present the nature of the adsorbing phase is not known. The mine waste itself is a complex mixture of primary and secondary minerals, including silicates and oxides and

would require a thorough characterization in order to estimate its pH dependent adsorption capacity. In general, (hydr)oxide surfaces would mainly carry a positive pH dependent charge under the conditions in this study why adsorption of negatively charged fulvate complexes would be enhanced (Stumm 1992). The conditions are more complex concerning the silicates.

Preliminary studies on the properties of the bark compost indicate a specific adsorption capacity of Cu(II) in the range of 0.1 meq g^{-1} at pH 5. A slightly lower capacity was found for zinc while for lead it was only 0.001 meq g^{-1} . These findings support the observations from the pot experiments where the lead concentrations increased with time.

The speciation of both copper and lead in the solution phase would be dominated by their complexes with humic substances according to geochemical modeling. At this point of the study the only plausible explanation for their different behavior would be that they associate with organic ligands that are retained differently in the substrate. Hence, more attention is paid to the chemical properties of potential organic ligands but also to their physical stability. In the pot experiments the ionic strength, and particular the calcium concentrations, are high enough to induce coagulation/aggregation of high molecular humic substances. Therefore also the potential physical entrapment of the carrier phases must be evaluated.

After the first summer the different treatments had very limited impact on the composition of the leachates and the bark compost dominated the composition (Karlsson *et al.* 2012a b). During the second summer there are indications for more complex quality differences of the DOC between the treatments. In general there is a tendency for a higher abundance of metabolically derived LMWOC. This raises the question whether they originate from microbial decomposition of the compost that would limit the systems adsorption capacities.

Conclusions

The UMBRELLA concept proved to sustain the growth of *Agrostis capillaris* on historic sulphidic mine waste, so far for a minimum of two seasons. Addition of bark compost lowered the concentrations of dissolved Al, Cd, Cu, Fe, Mn, Ni and Zn significantly. The DOC concentrations governed the behavior of the elements and the major component in the DOC had a molecular weight in the fulvic acid range. The concentrations of Ca and Pb increased nearly to those in leachates from unamended waste.

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