# The effects of organic acids on the leaching of heavy metals from mine tailings

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## Abstract

A laboratory study was conducted to determine whether the concentration of heavy metals, zinc (Zn), lead (Pb), and cadmium (Cd), in leachate from mine tailings could be affected by the presence of organic acids exuded by plant roots and microbes in the rhizosphere. Geochemical modeling predicted that some organic ligands found in the rhizosphere have the capability to complex and increase the solubility of Zn. These results were confirmed by batch and column studies in which mine tailings were exposed to 0–10000 $\mu M$ organic acids. The leachate was analyzed for Zn, Pb, and Cd content and for organic acid concentration.

## 1. Introduction

Mining activity in SE Kansas generated large piles of heavy metal contaminated mine tailings that were deposited on the ground surface. Water and wind erosion has produced runoff and leachate that has contaminated both surface and groundwater causing health hazards [1]. One method of stabilizing and reclaiming these sites is revegetation since proper soil cover can eliminate surface erosion and the plants' demand for water can restrict leaching. Soil amendments such as fertilizer, manure, sewage sludge, or lime are used to help stabilize the area and promote plant growth. The addition of topsoil is not preferred due to the high cost involved. Establishing plants directly in the mine tailings without topsoil is much more cost effective and less disruptive to surrounding areas [2].

The effect of vegetation on the movement of heavy metals from heavy metal contaminated soils is not fully understood. Direct contact between plant roots and contaminated material may increase the probability for leaching heavy metals. The exudates from soil microorganisms and roots of higher plants contain organic acids,

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some of which are part of the tricarboxylic acid cycle: pyruvic, citric, cis-aconitic, isocitric, oxalosuccinic, α-ketoglutaric, succinic, fumaric, malic and oxaloacetic. Other fatty acids commonly found in the rhizosphere are formic, acetic, propionic, and butyric. Also, found are oxalic, glycolic, lactic, and tartaric. Higher plants contain aromatic acids including cinnamic, p-coumaric, caffeic, ferulic, melilotic, proto-catechuic, and gallic. Plant growth regulators containing carboxylic acid groups, such as indoleacetic acid, are exuded from plant roots and are found in plant residues [3].

Bacteria and fungi produce different types of organic acids. Simple volatile acids (formic, acetic, propionic, and butyric) are produced by bacteria while fungi produce nonvolatile acids such as fumaric, succinic, lactic, and malic [3].

Sugar acids are another type of acid produced by microorganisms. Examples of these are: gluconic, glucuronic, galacturonic, and 2-ketogluconic acids. Aromatic acids produced by microorganisms include ferulic, vanillic, syringic, p-hydroxy-benzoic, and p-hydroxycinnamic [3].

Organic acids in soil are in continual cycles of synthesis and degradation. The concentration of acid in soil is a balance between these processes. Longer chain fatty acids may be more persistent because they have lower solubility and are strongly adsorbed to the clay and humus particles. Typical concentrations of some of these acids are: formic, 2–5 mM; oxalic, 0.05–1.0 mM; and citric, up to 0.05 mM [4]. Organic acids and their degradation products may provide ligands or chelating agents for the heavy metals in the solid phase.

Pohlman and McColl studied the effect of organic acids on the mobility of metals from forest soils and the dissolution of soil minerals [5, 6]. Acids identified as leaching aluminum are oxalic, malic, citric, protocatechuic, and salicylic, with hydrogen ions released by the carboxylic acid groups playing a major role in metal dissolution. Functional group positions and types were most important in determining if an organic acid would complex metals and increase leaching. The pH of the input acids varied from 3.0 to 5.65 and pH was not reported for the leachates.

Manley and Evans [7] studied the effect of organic acids on the dissolution of feldspar, an aluminosilicate mineral and common component of soil. Acids studied were citric, oxalic, salicylic, protocatechuic, gallic, p-hydroxybenzoic, vanillic, and caffeic. The dissolution of feldspar was greatest for citric and oxalic acids. Concentrations used in this study were $10^{-1}$–$10^{-5}$ M and were not pH adjusted.

A greenhouse study of the effect plants have on the leaching of zinc (Zn) from a heavy metal contaminated mine tailings and soil mixture showed that greater amounts of Zn were leached when plants were present [8]. This study also looked at the role that mycorrhizae fungus plays in the leaching of Zn. The samples inoculated with mycorrhizae fungus leached less Zn than those that had not been treated. Samples with plants leached more zinc compared to those without plants. Specific leaching mechanisms were not investigated.

Another study used heavy metal contaminated mine tailings packed in columns. These vegetation free columns were leached with different organic acid solutions to study the interaction of organic ligands and the heavy metal in the mine tailings [9]. Columns were packed with a layer of contaminated mine tailings and a layer of uncontaminated soil. These were leached under saturated flow conditions. The

amount of Zn in the leachate was monitored as a function of time for different acids of varying concentrations. After initially high concentrations of Zn in the leachate, the concentration of Zn decreased sharply. It was suggested that this change was due to microbial activity. As the acid solution flowed through the columns, microbes degraded it to varying amounts. The amount of Zn leached varied proportionally to the concentration of unaltered acid in the leachate.

Each of the above studies looked at the effect of organic acids on the leaching of heavy metals. In those studies the interaction of heavy metals and soil was not considered separately but as part of the experiment. The objective of this research was to quantify the effect of rhizosphere organic acids on the leaching of heavy metals from mine tailings containing elevated levels of zinc, lead, and cadmium. This study concentrated on the mine tailings and organic acid interactions and did not include soil.

## 2. Procedures

Contaminated mine tailings from the Galena, Kansas area were used in the study. The mine tailings, also called 'chat', consisted of coarse to sand-like material resulting from the processing of mined ore. The total concentrations of heavy metals in the mine tailings were: 13 700 mg/kg zinc, 1150 mg/kg lead, and 89 mg/kg cadmium. These concentrations were highest in the sulfide and carbonate fractions, and a significant concentration of this was in sorbed and exchangeable fractions [10]. The pH of the mine tailings was between 8.2 and 8.5.

### 2.1. Batch studies

Concentrations of Zn for each acid type and concentration in equilibrium (or steady state) with the mine tailings were determined using laboratory batch studies. Twenty milliliters of acid solution and 10 g of chat were placed in flasks and shaken for 2 h. In preliminary experiments, ranging in duration from 0.5 to 24 h, we found 2 h to be adequate to establish steady-state concentrations. The solution was filtered through 42 Whatman filters and analyzed for heavy metal concentration by atomic absorption.

### 2.2. Column studies

Columns were constructed of PVC pipe sections 4 in diameter by 6 in length. The mine tailings were sieved through a 2 mm screen, and 600 g was packed into each column leaving a pore volume of 100 ml. The bottom and top of the columns had layers of plastic mesh netting and glass wool to prevent the loss of tailings into the leachate. Flow to each column of 0.04 ml/min was provided by a peristaltic pump. The columns were kept under saturated flow conditions with the flow entering the bottom and exiting the top. Leachate was collected periodically for each column.

## 2.3. Geochemical modeling

A chemical equilibrium model, MINTEQA2 [11], was used to predict the aqueous phase speciation and solid-phase formation/dissolution of the mine tailings exposed to the organic acids. MINTEQA2 is thoroughly documented for mathematical approach and thermodynamic database. We assumed that leaching solutions were in equilibrium with $CaCO_3$, atmospheric $CO_2$ (0.0003 atm), $ZnCO_3$ (smithsonite), $Al(OH)_3$ (amorphous), and constant $Cl^-$, $SO_4^{2-}$, $H^+$, and ionic strength. Complexation constants for many organic acids of interest were not available in the MINTEQA2 database. Constants were obtained from Martel and Smith [12], corrected to an ionic strength of 0.0, and added to the model. The effects of organic acids on the leaching of heavy metal from the mineral solids were evaluated, by examining the changes in total soluble metal concentration.

## 2.4. Organic acid preparation

The organic acid solutions were prepared in three concentrations: 10 000, 1000, and 0 μM. The influent organic acid solutions used in this study were prepared using a stock solution and distilled, deionized, sterile water. The acids were filtered through 0.22 μm filters to ensure the sterility of the solutions. Solutions were refrigerated prior to use. Most of the organic compounds are susceptible to decomposition by organisms present even in distilled, deionized water; therefore, the previously mentioned sterilization steps for influent solutions and leachate samples were critical to reduce losses of organic acids. The pH of the solution was adjusted to 7.0 by the addition of MgO. By adding $MgCl_2$ as needed, constant magnesium concentration was maintained for all influent solutions. Magnesium was used as a divalent cation to prevent the dispersion of the chat during the experiment. Usually, calcium is the divalent cation used, but calcium forms a sparingly soluble phase with oxalate.

## 2.5. Organic acid analysis

Leachates were filter-sterilized to prevent degradation of the organic acids by microorganisms before analysis. Filtered samples were refrigerated while waiting for analysis. Organic acid concentrations were analyzed by a Dionex 2110i Chromatograph with a Dionex HPICE-ASI column and Anion micro-membrane suppressor. The eluent solution was 1.0 mM octane sulfonic acid flowing at a rate of 0.7 ml/min. The column pressure was 460 psi, and an HPICE-AS1 guard column was used. Regenerant was tetrabutylammonium hydroxide, sodium salt, at a concentration of 5.0 mM and a flow rate of 3 ml/min. Regenerant and eluent were prepared daily.

## 2.6. Heavy metal analysis

Filtered leachate samples were analyzed for heavy metal concentrations using a Perkin–Elmer 460 Atomic Absorption Spectrophotometer (AA) and an air/acetylene flame. Stored samples were acidified to prevent precipitate formation.

## 3. Results and discussion

Geochemical modeling and batch results for formic, succinic, oxalic, and citric acid are shown in Table 1. Of the acids studied, modeling predicted that citric acid would be the greatest complexor of zinc, as compared to formic, succinic, and oxalic acid. Although the complexation constants for Zn-oxalate and Zn-citrate are of similar magnitude, most of the oxalate in solution is precipitated as Ca-oxalate (with Ca coming from $CaCO_3$). As a result, very little oxalate remained to complex Zn. Succinate is predicted to increase Zn solubility slightly when the succinate concentrations are high; neither formate nor succinate is expected to increase appreciably the leaching of Zn. These results were supported by the batch study.

In the column study, the concentration of zinc leached varied with time, acid type, and concentration. High initial concentrations of zinc were washed from the columns as saturated flow started. The concentration of Zn decreased to a lower level after 2 to 3 pore volumes of flow through the columns. The amount of Zn leached in the columns was similar for the formic and succinic acids and the $0.0\,mM$ control concentration (Figs. 1–3). Fig. 4 shows that oxalic acid leached slightly more zinc than the formic and succinic acids. Citric acid leached the most zinc from the chat. Citric acid also had the largest initial flush of Zn at 42 ppm (Fig. 5). As the concentration of citric acid was decreased, less zinc was leached as seen in Fig. 5. Oxalic acid followed a similar trend (Fig. 4). As noted in Section 2, oxalic acid forms a low-solubility solid compound with calcium. Since the chat material also contained calcium carbonate, some oxalate formed calcium oxalate in the columns. This further decreased the amount of oxalate available for complexing zinc.

Complexing reactions depend on several factors: (1) the diffusion rate of the complexing agent or ligand from the bulk phase to the reaction site; (2) the amount of contact time between the ligand and the reaction site; (3) the degree of dissociation of the organic acids in solution; (4) the type and position of functional groups on the organic acids; and (5) the chemical affinities of the chelating agents for the metals involved [5].

Table 1

Aqueous phase zinc concentrations in ppm from geochemical modeling and batch study to obtain equilibrium results for chat from SE Kansas

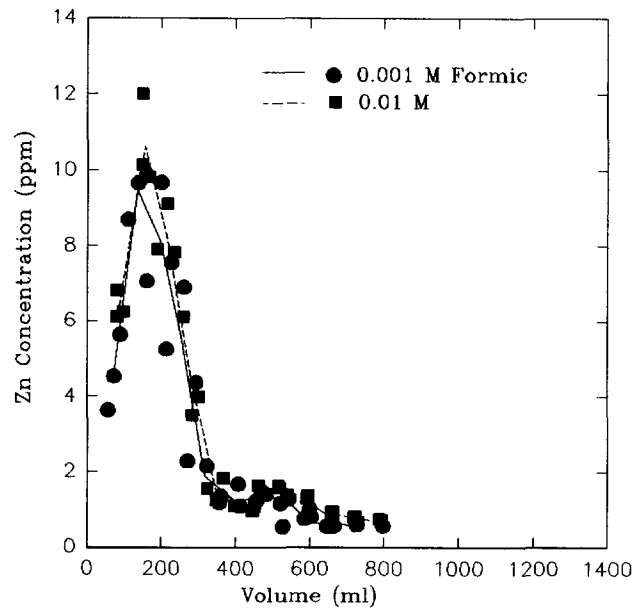| Acid | Formic | | Succinic | | Oxalic | | Citric | |
|---|---|---|---|---|---|---|---|---|
| Concentration (mM) | Model | Batch | Model | Batch | Model | Batch | Model | Batch |
| 0.0 | 3.4 | 1.9 | 3.4 | 1.9 | 3.4 | 1.9 | 3.4 | 1.9 |
| 0.1 | 3.4 | 2.2 | 3.4 | 1.9 | 3.8 | 2.1 | 10.5 | 2.0 |
| 1.0 | 3.4 | 1.7 | 3.4 | 1.8 | 3.8 | 1.8 | 32.0 | 9.8 |
| 10.0 | 3.4 | 2.0 | 4.0 | 2.8 | 3.8 | 2.7 | 281.2 | 30.7 |

Fig. 1. Zinc concentration in leachate from columns receiving formic acid.
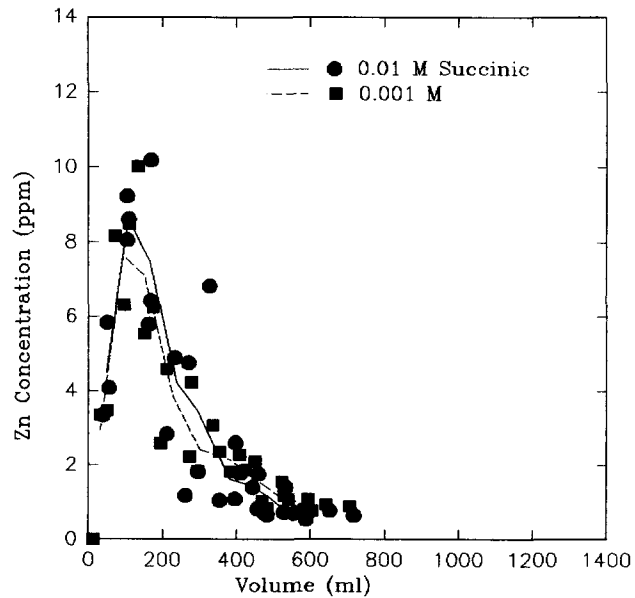


Fig. 2. Zinc concentration in leachate from columns receiving succinic acid.
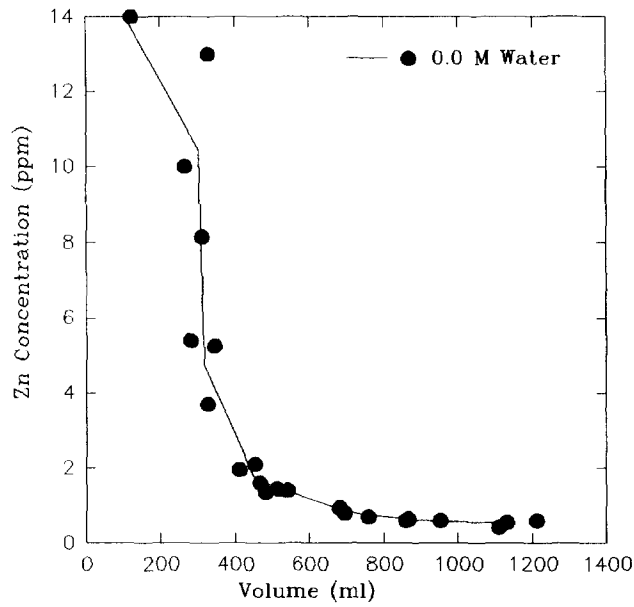
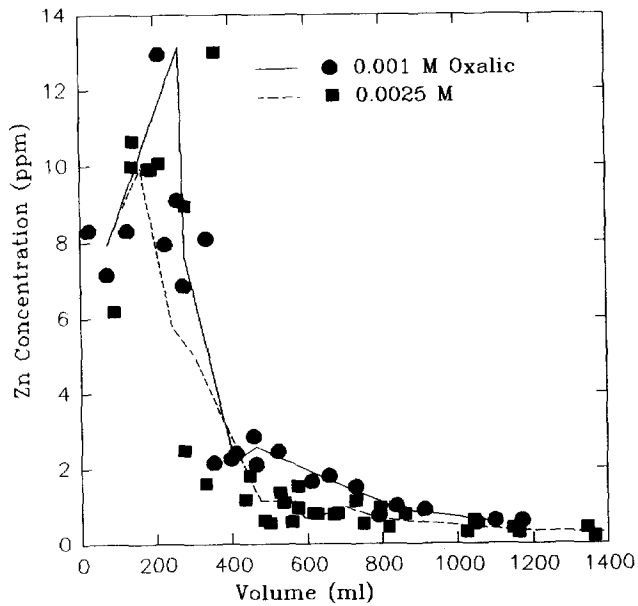Fig. 3. Zinc concentration in leachate from the control columns.



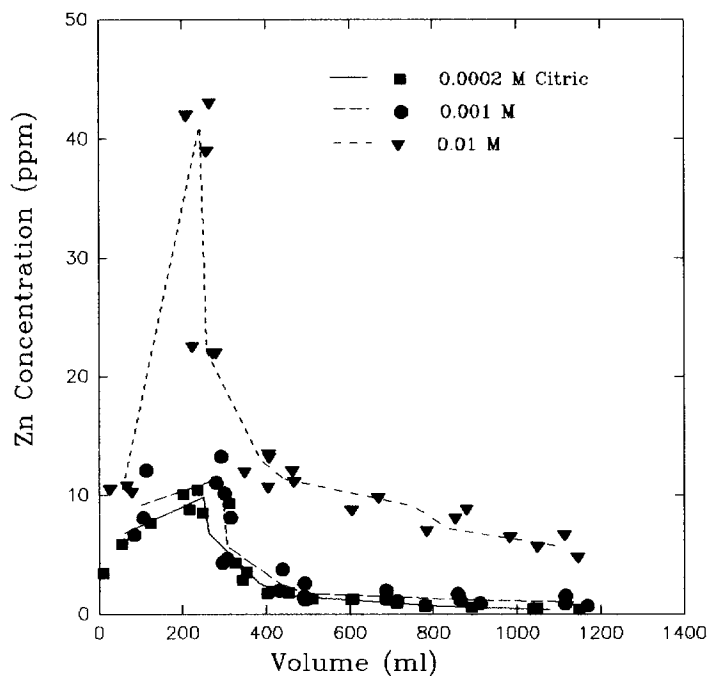Fig. 4. Zinc concentration in leachate from columns receiving oxalic acid.

Fig. 5. Zinc concentration in leachate from columns receiving citric acid.
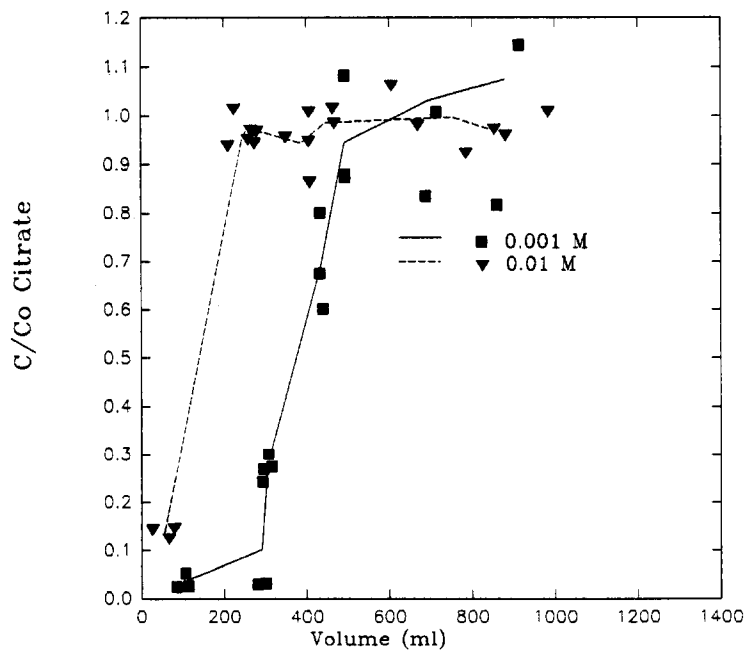


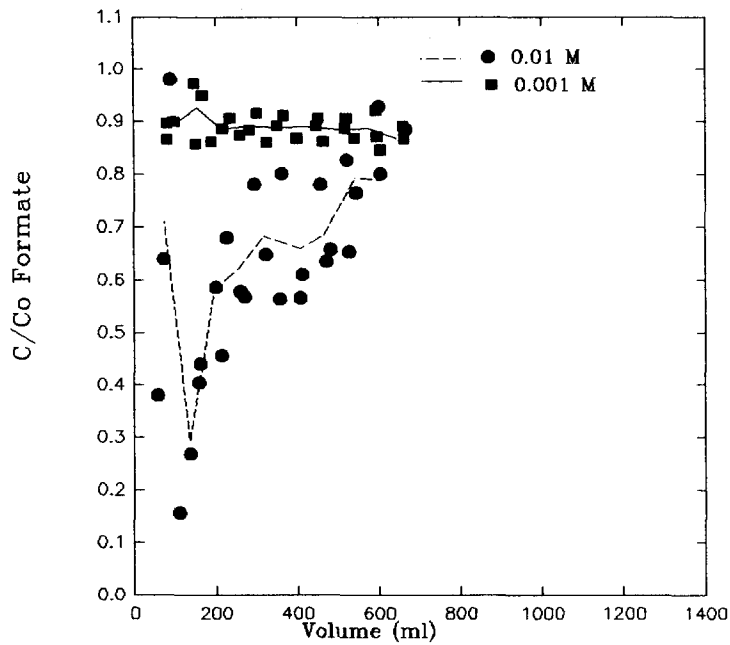Fig. 6. Acid concentration in leachate from columns receiving citric acid.

Fig. 7. Acid concentration in leachate from columns receiving formic acid.
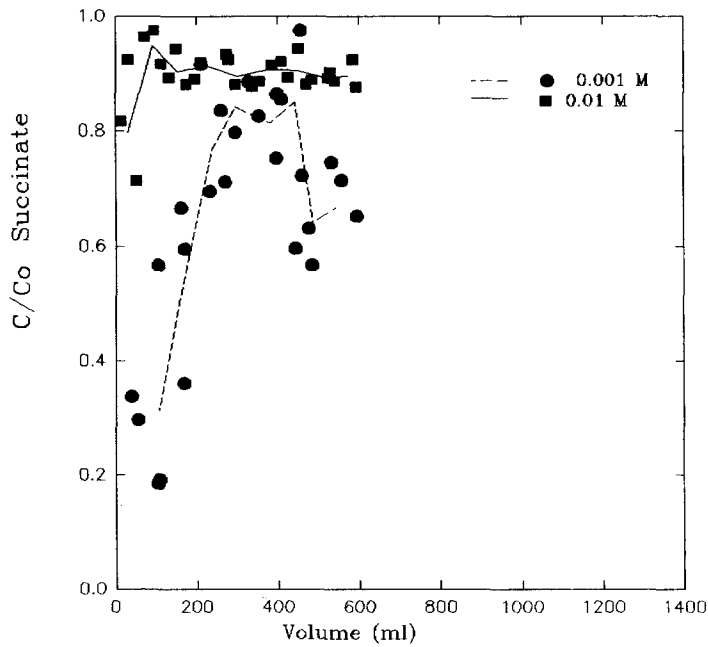
Fig. 8. Acid concentration in leachate from columns receiving succinic acid.

Since lower concentrations of oxalic acid resulted in a slightly higher concentration of zinc leached, the contact time between oxalate and the reactive sites may be greater. The effect of functional group and position predicted which acids would or would not be complexors of zinc. These results were similar to those reported by Pohlman and McColl [5, 6], and Manley and Evans [7].

Concentrations of acid in the leachate were measured for formic, succinic, and citric acids. These concentrations in the leachate were initially undetectable or very low. As the experiment progressed, the acid concentrations approached the initial influent concentration (Figs. 6–8). This trend was opposite of that shown by the Zn concentrations in the leachate. When the Zn concentrations in the leachate were high, the acid concentrations were low and vice versa. Initially, the acids are dissipated greatly when interacting with the chat. As the type of Zn available at the surface sites of the chat changes, the acids are dissipated to a lesser extent.

## 4. Conclusions

The establishment of vegetation on mine tailings would reduce wind and surface erosion but may increase the amount of heavy metal leached, and by that increase the groundwater contamination. In this study the presence of rhizosphere organic acids did affect the mobility of zinc from heavy metal contaminated mine tailings. Overall, citric acid released more zinc than formic, succinic, and oxalic acids and it was predicted to be a complexor of zinc by the modeling study. The highest concentrations of zinc in the leachate occurred for the highest concentration of citric acid. For all three acids and the water control, the highest zinc concentrations were leached at the onset of the experiment, with the concentration settling to a lower value after 2 to 3 pore volumes of flow. The acid concentration in the leachate showed an effect opposite to that of the zinc concentration. Initially, the acid concentration was very low, then it increased to near the influent concentration, mirroring the zinc concentration in the leachate. Further study is recommended on the effects of other natural rhizosphere organic compounds on the mobility of heavy metals from contaminated mine tailings and on the effect plants have on the availability of water for leaching events in a vegetated system.

## Acknowledgements

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