

Leaching of Trace Metals from Soil under Alternating Oxidic-anoxic Conditions: a Column Study

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Abstract. One of the most important and abundant transition metals in the Earth’s crust is iron, which plays a key role in environmental biogeochemistry. A large number of trace metals and other contaminants are associated to Fe(III) minerals; under anoxic conditions, Fe(III) can be reduced and, consequently, potentially dangerous compounds can be released. In this work we present column experiments of metal mobilization from soils sampled from a mining area in Northeastern Romania. A preliminary study was carried out to determine the extractability of metals in CaCl₂ 0.01 M solution and the influence of adding 1 g L⁻¹ lactose as a carbon source. The results showed that the heavy metals were rapidly brought into solution in the medium supplemented with lactose. Then, the release of metals was studied using columns packed with soil percolated with the CaCl₂ solution. It was observed that, while Zn and Pb are released in the solution congruently with the reduction of Fe and Mn, copper is mobilized immediately and can be found in the leachate. This suggests that, under alternating oxidic-anoxic conditions, the soil can become a source of contamination.

Key words: Column study, heavy metals, leachate, redox transformations

Introduction

Metal mining, smelting, industrial processing and waste disposal result in heavy metal inputs into the environment. Heavy metals are sorbed and retained by the soil, leading to their accumulation. However, the capacity of soil to store these toxic metals is, unfortunately, not infinite (Bridges and Van Baren, 1997). Unlike most other organic pollutants, heavy metals cannot be degraded chemically or biologically. Part of the retention capacity of the soil relies on Fe and Mn oxides that can adsorb the metals on their surface or incorporate them into their mineral structure. Under anaerobic conditions, however, microorganisms can interact with the oxides. As a result Fe and Mn oxides become more soluble and bring the metals that are associated with them into solution.

Usually the organic substrates in the soil system act as electron donors coupled with ionic substances (Marsh and McInterney, 2001). For example, Ayyasamy and Lee (2009) studied the influence of glucose, humic acid and ADQS (anthraquinone-2,6-disulphonate) on the release of heavy metals from soil columns, in the

presence of *Shewanella sp.* They concluded that the highest rate of dissolution of heavy metals in soil was higher in the experiments carried out with glucose (30 mM) and ADQS (1 mg L⁻¹) as an electron transporter.

Column tests prove to be a useful tool for understanding the behaviour of heavy metals in soil, especially their mobility, transport and fate. Jean-Soro et al (2012) evaluated the leaching of metals from an industrial soil using citric acid and EDTA by column studies. The mobility of heavy metals in two different types of soil using column tests was assessed also by Kowalkowski et al (2010), using CaCl₂ 0.01 M as the leaching solution.

As pointed out by Borch et al. (2010), the quantitative understanding of contaminant fate in fully oxidic soils or permanently reducing environments has received much interest in research studies. However, far less attention has been given to the biogeochemical functioning of systems characterized by fluctuating conditions. Microbiological communities, mineral assemblages and redox species may differ greatly from those encountered in permanently oxidic or anoxic environments. The aim of this work is to study the effects

of redox changes on contaminant release and transport.

Materials and Methods

Two soil samples were obtained by mixing 5 subsamples collected at a depth of about 20 cm. The sampling point is a mining area in the Eastern Carpathians, Romania, where copper ore had been extracted over a long period of time. The samples were air-dried and then passed through 2 mm sieve. For chemical analysis, the soil was ground up to pass through 0.5 mm stainless steel mesh.

The texture of the soil samples was determined and the soils were classified as loam/sandy loam. Other properties are detailed in Table 1. The soil pH was determined after 2 h agitation at 180 rpm and 15 min sedimentation of a suspension of 10 g of soil in 25 mL of KCl 1M. The organic content of the soil (and C/N ratio) was also determined.

Table 1. Selected soil properties

Sample	pH	Humidity %	C %	N %
B1PS	4.85	2.5	2.7	0.26
B2PS	5.24	2.6	4.8	0.42

The soil pseudo-total content of Fe, Mn, Cu, Zn and Pb was determined after an acid digestion procedure using 10 mL *aqua regia* (HCl:HNO₃ 3:1 v/v) in a Teflon beaker which were added to 1 g of soil, digested at room temperature for 16 h and then heated in a microwave oven at 180°C for 20 min. The mixture was then transferred quantitatively to a volumetric flask and made up to 50 mL with deionized water. The metals were analysed by flame atomic absorption spectrometer. The extractions in *aqua regia* were carried out in duplicate.

Batch tests were also performed for the extraction of heavy metals from soil using DCB (dithionite-citrate-bicarbonate) and ammonium oxalate. Fifty mL of the prepared solutions were added to 1 g of soil, shaken for 16 h at 180 rpm, centrifuged and analysed by FAAS. DCB is expected to extract the so called free-iron i.e. the Fe which is not in the silicate minerals. The ammonium oxalate at pH 3 complexes Fe and Al of the amorphous oxides and associated to the organic substances.

Since the location and the physico-chemical characteristics of the soil were similar, the soil samples were mixed and 20% (v/v) of perlite was added to increase the porosity of the soil and facilitate the

percolation. The metals in the mixed soil were extracted with CaCl₂ 0.01M by adding 30 mL solution to 10 g of soil, shaking for 2 h at 180 rpm, centrifuging and analysing by FAAS.

Column tests were performed during 23 days in 70 cm high and 7 cm diameter Plexiglass columns. Two columns were filled with 1850 g mixture of soil and perlite each and a volume of 1300 mL of CaCl₂ 0.01M and lactose 1 g L⁻¹ was added from underneath, so that the soil would be completely submerged. Anoxic conditions were obtained by flushing the columns with N₂ for about 30 seconds, then they were closed tightly to avoid entrance of air. The columns are equipped with 2 rhizon samplers each, at two different heights, the higher at 15 cm and the lower at 30 cm depth from the surface of the soil, in order to assess the mobility and transport of heavy metals in the soil solution. Also, the bottom of the columns were provided with filters to avoid loss of material during the periodic leaching.

The soil solution was sampled using the lower and the higher rhizon samplers during the 2nd, 7th, 10th, 14th, 16th, 21st and 23rd days of the experiment and the percolations, i.e. emptying of the column, were performed in the 2nd, 9th, 16th and 23rd day of the experiment. Eh and pH of the leachate were also monitored. After each percolation, the soil was kept under oxic conditions for three days then the columns were refilled with the volume of fresh solution that had been extracted.

Results and Discussion

The preliminary results show that the concentration of heavy metals extracted with *aqua regia* are higher than normal values in soil, which might be due to anthropogenic activities or to the parent rock. DCB extraction gives information on the amount of metals that could be mobilized from the soil, while oxalate points out the concentration of metals in amorphous state or linked to organic substances. The values are summarized in table 2.

The amount of Fe, Mn, Zn, Cu and Pb in the 0.01 M CaCl₂ solution was 0.3, 6.6, 1.0, 0.2 and 0.4 mg kg⁻¹, respectively. The addition of lactose enhances the release of metals, as compared to the single use of CaCl₂ (Fig 1). This is also confirmed by the work of Ayyasamy and Lee (2009), who used glucose in the presence of *Shewanella sp.*, with better results than without the carbon source.

Table 2. Concentration of metals in soil extracted with different reagents (AR – *aqua regia*, DCB – dithionite-citrate-bicarbonate, Ox – oxalate)

Sample	Fe (g/kg)			Mn (mg/kg)			Cu (mg/kg)			Zn (mg/kg)			Pb (mg/kg)	
	AR	DCB	Ox	AR	DCB	Ox	AR	DCB	Ox	AR	DCB	Ox	AR	DCB
B1PS	41.5	11.8	4.7	1719	615	434	64.5	11.3	28.7	119	68.8	6.8	37.6	3.9
B2PS	43	11.2	5.3	1254	690	605	139.7	33.3	83.8	176.4	87.5	39.8	54.9	14.8

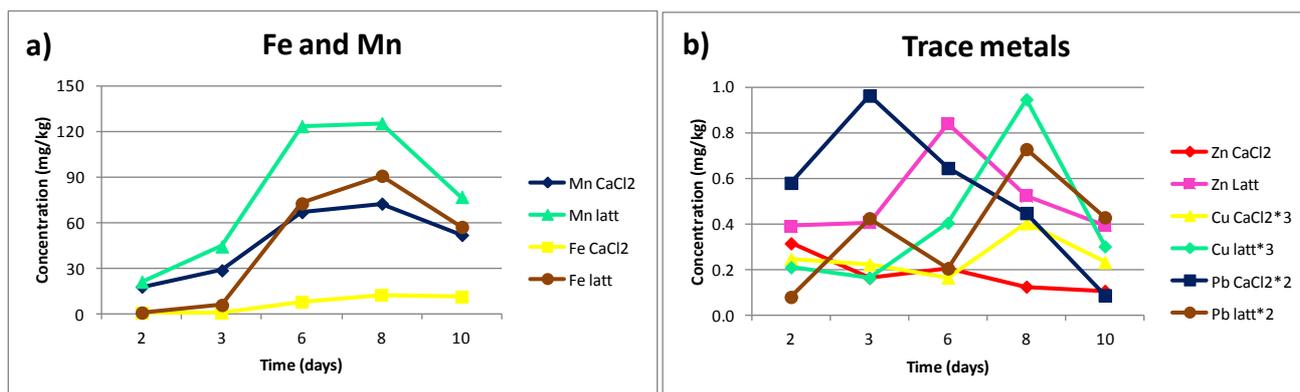


Fig. 1. Different release of Fe, Mn (a) and Zn, Cu and Pb (b) by means of CaCl₂ and CaCl₂ with lactose.

The influence of lactose on the redox transformations in soil is suggested by the decrease in Eh after only three days of contact with the solution, while, in the absence of the carbon source, the reduction occurs in a much slower pace (Fig 2). The rate of mobilization of heavy metals increased drastically when the solution had a low redox potential.

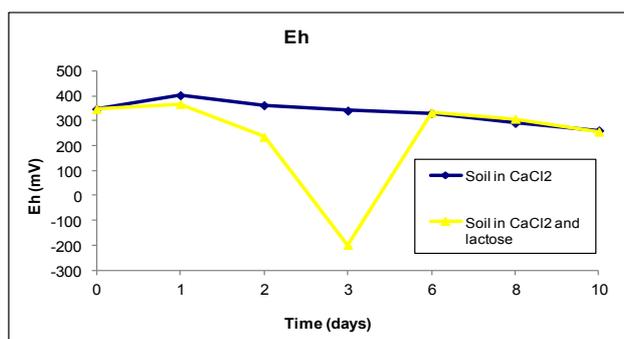


Fig. 2. The effect of lactose on the redox potential of the soil.

The solubility and mobility of metals in the soil columns was monitored during the 23 days of the study. The results showed that the mobilization of iron and manganese occurred and increased concentrations were observed in the samples taken from the lower rhizon than the higher one, with Fe II trend dependent on the phases of filling/emptying the columns with solution (Fig 3). The system presented an oscillating behaviour regarding the metal release, consistent with the results of Di Palma and Mecozzi (2010). These variations may indicate that equilibrium conditions were not achieved.

A similar trend was observed for both Pb and Zn, suggesting that reduction processes in soil causes the mobilization of elements with which iron formed mineral associations. Copper showed an opposite behavior, with concentrations decreasing constantly in the samples collected from the rhizon, as compared with reduced iron. However, in the percolated solution, Cu was the metal whose concentration increased dramatically during the entire period of the experiment (Fig 4). This suggest that soil submerged for a length of time similar to the one

experimented can become a source of Cu contamination for the groundwater.

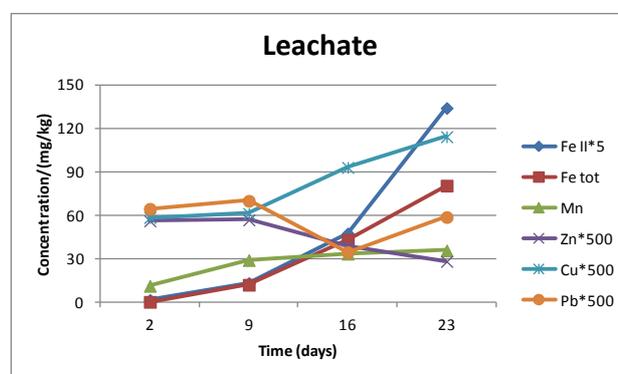


Fig. 4. Metal variability in time in the solution leached from the soil column

Conclusion

Batch and column tests performed on a soil affected by mining activities have pointed out that metal mobilization may be generated by the variation of ambient parameters such as lowering the redox potential and increasing the amount of carbon in soil. The rate of heavy metal release was higher in solution containing 1 g L⁻¹ lactose than just CaCl₂ 0.1 M. Among the metals in the soil, Fe and Mn showed higher levels of dissolution and a clear transport to the lower part of the column than the other heavy metals. Fe and Mn tend to co-precipitate with the other components under aerobic conditions in easily soluble forms which are dissolved in the following anoxic step. This mechanism improved significantly the release of the other metals.

In conclusion, soils submitted to successive aerobic-anaerobic conditions, may release heavy metals in the environment, potentially acting as sources of contamination.

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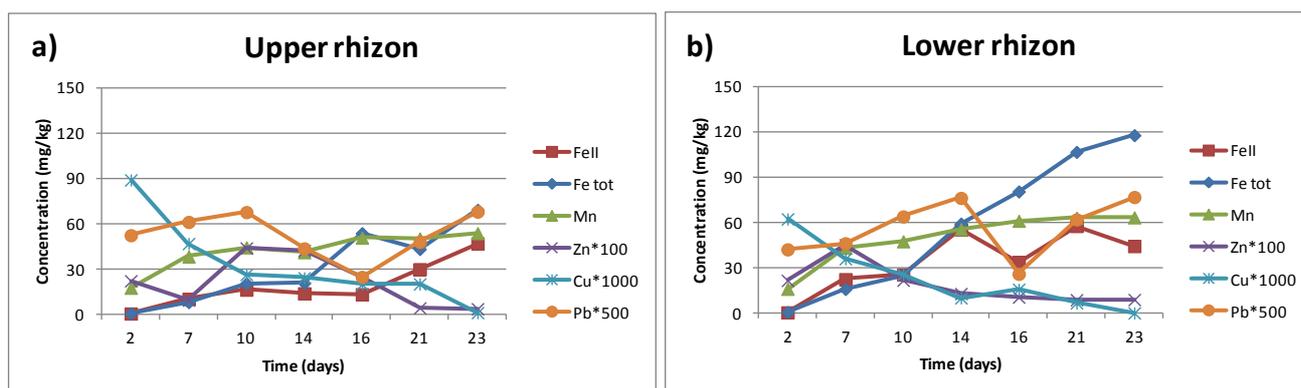


Fig 3. Metal variability in time in the solution extracted from the upper rhizon (a) and lower rhizon (b).

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