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RELEASE OF HEAVY METALS IN FLOODED SOILS: EFFECT OF LABILE ORGANIC C ADDITION

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The reductive-dissolution of soil Fe and Mn oxyhydroxides might cause the release of heavy metals associated with them. This process is generally microbially-mediated. The solubilization of metal hydroxides was enhanced by the addition of lactose (low-molecular-weight organic matter) as an electron donor and the release of Cu and Zn was monitored. The results showed that the added labile C led to a fastened onset of anoxic conditions, therefore an increased rate of Fe and Mn reduction which, in turn, led to augmented release of heavy metals. This should be considered when fertilizers are added to soils which may suffer flooding.

Keywords: heavy metal release, Fe and Mn oxides, reductive dissolution, lactose

1. Introduction

One of the most frequent practices in agriculture is fertilization via addition of compost or manure to the soil. While the dynamics of dissolved organic matter (DOM) in soil are well described [1] and the characteristics of compost have been intensely studied [2, 3], little is known about the effect of low molecular weight organic matter (OM) on heavy metal release and mobility in soil pore water under reductive conditions. Some soils in temperate areas, in particular, have been suffering from flooding due to intense and frequent rain events [4]. This potentially leads to the onset of anoxic conditions in soils that are not normally waterlogged. The consequent reductive dissolution of Fe and Mn oxyhydroxides could, therefore, release metals that are associated with them.

The dissolution of Fe and Mn oxides is mediated by microorganisms even in anaerobic conditions. Hence, the metabolism of bacteria and other microorganisms cause, among others, the oxidation of organic matter (OM) and the reduction of Fe and Mn (hydr)oxides. Their reductive dissolution may release trace metals associated with them (adsorbed, co-precipitated, occluded, etc). Therefore, bioweathering under anoxic conditions could lead to the release of toxic heavy metals into the environment. Saturated soil environments may include ecosystems such as rice paddies, wetlands (swamps, marshes, and bogs) and compacted soils.

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Reducing conditions occur in soil when it is oxygen-depleted causing heterotrophic microbes to use other electron acceptors, like nitrate, manganese, iron, ecc. [5]. Although this may occur in case of large application of manure [6], the majority of soil reduction is caused by saturation or flooding. Soil can become flooded when it is poorly drained or when rainfall or irrigation is excessive. A major issue arises when reducing conditions arise from both organic fertilizer addition and submergence, due to the speed and enhanced effects of anoxia. The most significant result of flooding is the isolation of soil from atmospheric oxygen, which activates several biological and chemical processes that change the system from aerobic and oxidizing to anaerobic and reducing [7].

The main electrochemical changes that influence the chemistry and fertility of flooded soils and growing of crops such as wetland rice include: decrease of redox potential (Eh), pH increase in acid soils and decrease in alkaline soils, and increase in specific conductance and ionic strength of soil solution [8]. These factors can have opposing effects on the reductive-dissolution of Fe and Mn oxides, which also affects the release of heavy metals, depending on the type and amount of soil organic matter, clay and mineral content, and soil texture.

In relation to the availability of organic matter to microorganisms, the soil offers an environment where substrate availability is both limited and irregular. Even though the soil contains a significant amount of organic matter (such as root exudates, plant and animal residues or partially degraded products of microbial activity), mainly as humic substances, soil microorganisms can only utilise it very slowly [1].

As noted by Vespraskas and Faulkner (2001) [9], an abundance of readily decomposable organic matter promotes reducing conditions. If organic matter is present in flooded soil, reducing bacteria create the reducing conditions by consuming organic matter.

Among the different organic substrates or electron donors present or added to soil, those with a simpler molecular structure may be more easily used by microorganisms and thus lead to a quicker onset of reducing conditions. The aim of this paper was to study the potential increase in the release of heavy metals due to the addition of lactose.

2. Materials and methods

2.1. Soil sampling

The soil samples were collected from the river valley of the town of Balan, Harghita county of Romania. Mixed Cu-Pb-Zn deposits have been mined in this area for centuries and copper ore had been extracted and processed by flotation until 2004. During the long period of activity, the atmosphere, the waters and the soil have been contaminated with heavy metals. For this study, soils from pastures were taken from 0-20 cm depth. To ensure the representativeness of the plot, all samples were composed of 5 mixed and homogenized subsamples, four from the endpoints and one from the center of an area with the surface of approximately 400 m^2.

Samples B1 and B2 were collected approximately 200 and, respectively, 150 m uphill from the preparation plant. The distance between samples B3 and B4 was approximately 5, respectively 5.5 km (downhill) from the preparation plant. The samples were collected at different distances from the contamination source in order to assess the extent of the contamination and the influence of the distance on the speciation of heavy metals.

2.2. General soil properties

All samples were characterised phisico-chemically according to MIPAF (2000) [10]. First, they were air-dried, gently crushed and sieved to pass through a 2 mm sieve. A small portion of each sample was further ground for microwave-assisted (MILESTONE Start D) *aqua regia* (HCl:HNO3, 3:1 solution) digestion and pseudo-total metals (Cu, Fe, Mn, Pb and Zn) were determined by flame atomic absorption spectrometry (FAAS, Perkin Elmer AAnalyst 400). All analysis were carried out in duplicate and the results were accepted if the coefficient of variation was within 5%.

The soil pH was determined potentiometrically in a KCl solution (1M), 1:2.5 soil/solution ratio using a WTW inoLab 720 pH-meter. The partitioning of the soil particles into five size fractions was performed by the pipette method, using Na-hexametaphosphate. Organic carbon and total nitrogen contents were measured in duplicate by dry combustion with a CE Instruments NA2100 elemental analyser.

Considering their location, distance from the contamination source, similar properties and metal content, the 2 soil samples from uphill were mixed and homogenized, as well as the downhill ones. The samples obtained were denominated B1B2 and B3B4.

2.3. Batch experiment

The experiment was carried out by adding 50 mL of 10 mM $CaCl_2$ solution in one case, and 10 mM $CaCl_2$ + 3 mM lactose solution, in the other case, to 10 g of soil in dark glass containers. Anaerobic conditions were ensured by flushing them with N_2 and sealing them tightly. The extractant solution used was $CaCl_2$ because it has an ionic force similar to soil solution and avoids the dispersion of the soil particles. The aim of the experiment was to understand how lactose might speed up the reduction processes, the dissolution of Fe and Mn oxides and the release of heavy metals. The experiment was carried out in duplicate, on a period of 10 days.

The reduction-oxidation potential of the two solutions was measured periodically by the electrode method [11], using a silver: silver chloride electrode (CRISON 2001). Ferrous iron was determined by the 1,10-phenanthroline method [12] and measured using a UV/VIS spectrophotometer (HITACHI U-2000). The pH variation was also monitored using a WTW InoLab pH-meter. The release of metals (Cu, Fe, Mn, Pb and Zn) into solutions was measured by FAAS.

3. Results and discussion

3.1. Soil properties

The main physicochemical properties of the soil samples collected from the study area are presented in Table 1.

Table 1

Main physical-chemical properties of studied soil samples

Sample	pH in KCl	C_{org}, %	N_{tot}, %	Texture	Fe, $g \cdot kg^{-1}$	Mn, $mg \cdot kg^{-1}$	Cu, $mg \cdot kg^{-1}$	Zn, $mg \cdot kg^{-1}$
B1	4.85	2.7	0.26	Sandy loam/loam	41.5	1719.4	64.5	119.0
B2	5.24	4.8	0.42	Sandy loam	43.0	1253.8	139.7	176.4
B3	5.15	2.9	0.28	Sandy loam/loam	45.5	1134.4	120.6	123.5
B4	4.96	5.2	0.51	Loam	42.2	1145.0	63.0	137.4

The low pH of the soil is typical for mining areas where the weathering of the copper-bearing sulphide deposits causes the formation of acid mine drainage and the acidification of soils. Consequently, due to the exploration and exploitation of metal ores, elements from various minerals are released into the environment. In the studied area, the main source of iron is pyrite (FeS_2), for copper is chalcopyrite ($CuFeS_2$), zinc is released from sphalerite ($(Zn,Fe)S$) and lead originates from galena (PbS) [13-15].

The contaminated soil collected from the river valley of Balan town are generally sandy. The proportions of sand, clay and silt of the soil samples were plotted on the International Soil Science Society (ISSS) texture triangle (Fig. 1) and it was found that most samples are loamy.

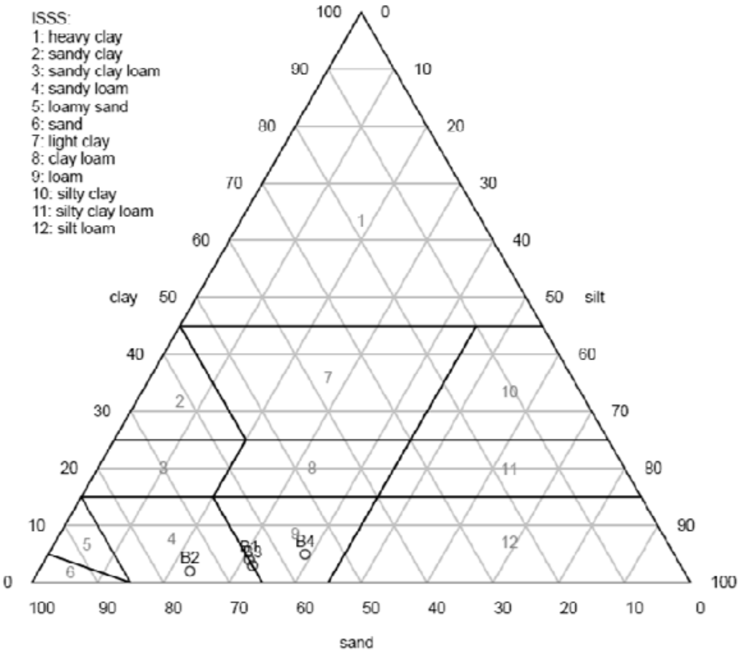

Fig. 1. Soil samples texture according to ISSS classification

3.2. Metal release during anoxic conditions

The experiments carried out in batch had the purpose to assess the effect of the addition of a carbon source (lactose) as an electron donor on the release of metals, under anaerobiosis. The results showed that the redox potential decreased much faster – in 3 days – in the solution containing lactose than in the one containing only $CaCl_2$ (Fig 2a). The Eh followed the trend described by Ponnamperuma (1972), as the redox potential fell rapidly after flooding, reached a minimum within a few days, rised rapidly to a maximum and then decreased with time [18]. How much the Eh decreases depends on the quantity of reactive electrons acceptors in the soil compared with the quantity of electrons generated by biological reactions such as organic matter oxidation. It also depends on the type and amount of microorganisms that are present. Bacteria that are consuming organic matter probably are the principal dynamic agents influencing redox potential [19].

Soil organic matter is a crucial factor in determining the onset of reducing conditions as it represents the main electron donor in soils. As reported by Craft (2001) [16], an abundance of readily decomposable organic matter appears to promote reducing conditions. Different kinds of organic matter may have a diverse influence on soil redox potential, according to their molecular weight, electron-transfer capacity, and availability to microorganisms. Under reducing conditions, metal-reducing bacteria have limited ability to metabolize high-molecular-weight compounds such as proteins, celluloses, or long-chain fatty acids [17]. In our case, the low-molecular-weight organic matter – the lactose – provided microorganisms with readily available C which boosted their metabolism and, consequently, the reducing conditions.

At the same time, the pH of the solution started to increase, which occurs in acid soils under anoxic conditions (Fig 2b).

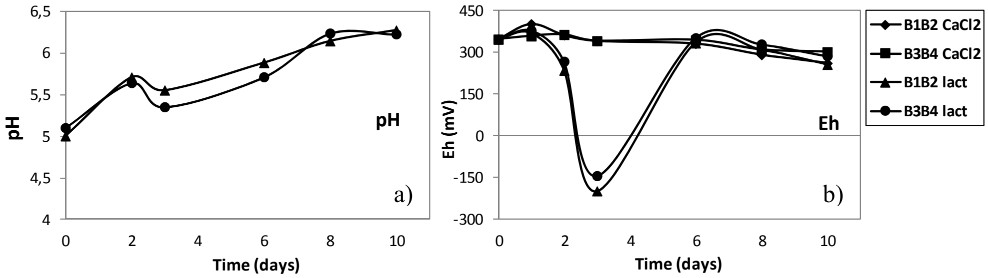

Fig. 2. Variation of soil parameters under anaerobic conditions: a) pH, b) Eh

Indeed, the reduction of iron and manganese from soil occurs with the consumption of H^+ which, in our case led to obtaining a pH of approximately 6.2 after 10 days of anoxic conditions. The pH of acidic soils increases following submergence because reduction reactions employ one or more hydrogen ions. However, the relationship between soil pH and soil reduction is not a simple one. Upon submergence, the production of acid radicals, especially -COOH and organic radicals may partly compensate for the pH-raising effect of reduction in acid soils or may cause further lowering of pH in the case of alkaline soils [20].

Iron was dissolved especially in the lactose-containing solution, where it was rapidly reduced (Fig 3a).

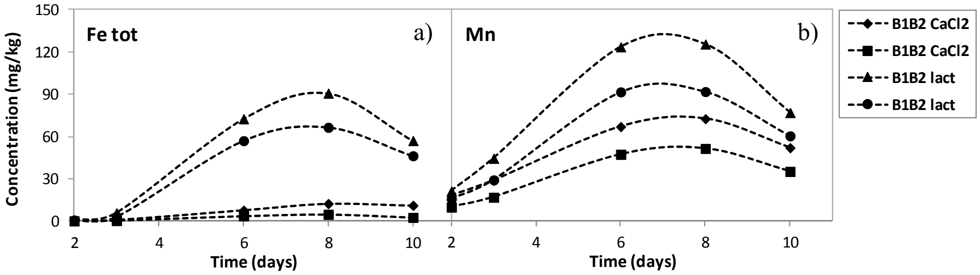

Fig. 3. Effect of lactose addition on the dissolution of a) Fe and b) Mn

Ferrous iron concentrations were almost equal to the total Fe, proving that all the Fe in solution was Fe (II) (data not shown). Due to the higher Eh and pH at which Mn is reduced, its release was faster than Fe and was enhanced by the addition of lactose (Fig 3b).

However, the redox potential of the solution had the lowest value earlier than the dissolution and reduction of Fe and Mn, suggesting that the initial Eh decrease and pH increase could have occurred due to rapid decomposition of soil organic matter (SOM).

Reducing conditions can cause a release of metals associated with Mn and Fe oxides following reductive-dissolution. This is an important mechanism that can potentially increase the soluble concentrations of metals: when reducing conditions cause the dissolution of hydrous Mn and Fe oxides, their associated metals can be released into the soil solution [21, 22]. Other authors have observed a decrease in the availability of heavy metals attributed to the increase of sorption of metals onto hydrous Mn and Fe oxides [23, 24] and formation of insoluble compounds with sulphide such as FeS_2, HgS, MnS, CuS [25]. The net effect of reducing conditions on the release of metals into solution depends, however, on the soil physicochemical properties, soil constituents and metal speciation.

In this experiment, the reduction of Fe and Mn oxyhydroxides caused the release of Cu (Fig 4a) and Zn (Fig 4b) in solution. While Zn release pattern can be related to the dissolution of Fe and Mn, Cu was found in solution later in the experiment. This can be due, on one hand to the fact that Cu might be bound to Mn oxides which are dissolved and release trace metals at a redox potential at which Fe is still in its ferric state and can retain metals [20]. Another suggestion is that Cu is associated with complex organic material or other systems that are not easily degradable. Oxidation-reduction reactions influence the speciation and the fate of contaminants, determining a modification in their availability and consequently in their potential environmental and human risk. The effect of soil reducing conditions on heavy metals solubility has important implications to both plant availability and toxicity, and chemical transport.

Similar results were obtained by Webb *et al*. (1998) [26], who used four different carbon sources, acetate, lactate, propionate and glycerol to remove heavy metals from natural and constructed wetland by production of sulphides. They observed that among the metals considered (Zn, Fe, and Mn) the bacterial growth and the rate of iron removal were higher using acetate and propionate.

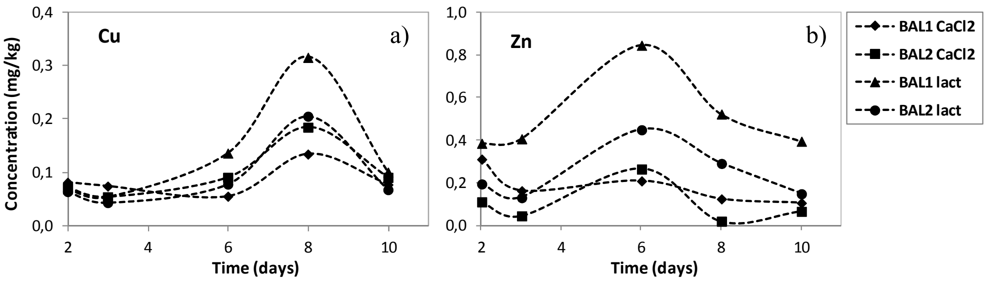

Fig. 4. Effect of lactose addition on the release of a) Cu and b) Zn

4. Conclusions

The results obtained in this study showed that the addition of a labile C source to a soil which may suffer flooding could be hazardous due to the rapid onset of reductive conditions. This situation may lead to the reductive-dissolution of Fe and Mn oxyhydroxides which may release the heavy metals associated with them, which would not occur in normal scenarios. Since the net effect of anoxic conditions on heavy metal mobility depends on the content of clay, organic matter, and sulphides, soil properties should always be considered when potentially flooded soils are to be fertilized.

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