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Mobilization of soil-borne arsenic by three common organic acids: Dosage and time effects

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HIGHLIGHTS

- Investigation into mobilization of soil-borne arsenic by low-molecular-weight organic acids.
- Oxalic acid was more dose- and time-efficient than citric and malic acids for As mobilization.
- Reductive Fe dissolution was more important than non-reductive reactions in liberating As.
- Soluble Ca could cause As re-immobilization by competing with Fe for organic ligands.
- Implications for understanding As behaviour in rhizospheric soil environments.

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ABSTRACT

A batch experiment was conducted to investigate the mobilization of soil-borne arsenic by three common low-molecular-weight organic acids with a focus on dosage and time effects. The results show that oxalic acid behaved differently from citric acid and malic acid in terms of mobilizing As that was bound to iron compounds. At an equivalent molar concentration, reactions between oxalic acid and soil-borne Fe were kinetically more favourable, as compared to those between either citric acid or malic acid and the soil-borne Fe. It was found that reductive dissolution of soil-borne Fe played a more important role in liberating As, as compared to non-reductive reactions. Prior to the 7th day of the experiment, As mobility increased with increasing dose of oxalic acid while there was no significant difference ($P > 0.05$) in mobilized As among the treatments with different doses of citric acid or malic acid. The dosage effect on soil-borne As mobilization in the citric acid and malic acid treatments became clear only after the 7th day of the experiment. Soluble Ca present in the soils could cause re-immobilization of As by competing with solution-borne Fe for available organic ligands to form practically insoluble organic compounds of calcium (i.e. calcium oxalate). This resulted in transformation of highly soluble organic complexes of iron (i.e. iron oxalate complexes) into slightly soluble organic compounds of iron (i.e. iron oxalate) or free ferric ion, which then reacted with the solution-borne arsenate ions to form practically insoluble iron arsenates in the latter part of the experiment.

1. Introduction

Soil-borne arsenic is a source of contamination to a range of receptors. Soil animals, microbes and plant roots could be directly exposed to arsenic when the soil-borne arsenic is mobilized and becomes available to them. The mobilized arsenic can be further transported from the soils to the above-ground portion of plants, surface water and groundwater, reaching off-site receptors. Therefore, understanding the mechanisms and kinetics of soil-borne arsenic mobilization is important for evaluating environmental risks from soil-borne arsenic.

In soils, arsenic tends to be bound to iron compounds through either formation of iron arsenate/arsenite or adsorption to iron oxides/hydroxides (Bowell, 1994; Goldberg and Johnson, 2001; Ma and Lin, 2012). Consequently, any soil processes that cause dissolution of As-bearing iron compounds are likely to result in mobilization of arsenic from soil matrix (Hartley et al., 2009; Wang et al., 2012). Low-molecular-weight organic acids (LMWOAs) are commonly present in soils, especially in rhizosphere as a result of plant root exudation (Strobel, 2001; Sandnes et al., 2005; Gadd

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et al., 2014). It has been well established that LMWOAs are capable of solubilizing iron oxides (Miller et al., 1986; Carson et al., 1992; Gerke et al., 1994; Jones et al., 1996; Reichard et al., 2007). However, little effort has been made to examine the effects of LMWOA-enhanced iron dissolution on mobilization of soil-borne arsenic.

Calcium is also a major element present in most of soils. Calcium can compete with iron for available low-molecular-weight organic ligands (LMWOLs) to form practically insoluble calcium-LMWOL compounds and consequently affect LMWOA-driven dissolution of iron oxides. While inhibition of LMWOA-enhanced iron dissolution by calcium carbonates in alkaline soils is well recognized (Ström et al., 2005), the complication of LMWOA-enhanced iron dissolution on As mobilization by non-carbonate-Ca in acidic soils has not been well addressed.

The concentration of LMWOAs is spatially and temporarily variable in soil environments (Jones et al., 2003; Renella et al., 2004; Boddy et al., 2007; Fujii et al., 2012; Jia et al., 2014). There is therefore a need to understand the mobility of soil-borne As as a function of LMWOAs concentrations and reaction time in order to better understand the complex processes related to LMWOAs-driven mobilization of arsenic in soils. Furthermore, LMWOAs have also been considered for uses as stimulants or agents for remediation of contaminated soils by heavy metals and metalloids, including LMWOAs-enhanced phytoextraction and soil washing (Agnello et al., 2014; Wang et al., 2014). To improve the effectiveness and efficiency of these remediation efforts, the time and dosage effects of LMWOAs on phytoavailability or mobility of soil-borne arsenic need to be sufficiently understood.

The objective of this study was to examine the effects of three common LMWOAs (citric acid, oxalic acid and malic acid) on the mobilization of soil-borne arsenic with a focus on two affecting factors (a) dosage level of each selected organic acid, and (b) reaction time. Attempt was also made to obtain insights into the mechanisms responsible for the observed phenomena and to understand the dynamics of pH, Fe, Ca and As in the soil solutions following various treatments with the LMWOAs.

2. Materials and methods

2.1. The soil samples used in the experiments

Three selected contaminated soil samples (M1, M2 and M3) were used for the experiments in this study. These samples were collected from the surface layers (0–10 cm) of soils at the Moston Brook closed landfill site in the Greater Manchester region, northwestern England. Detailed information on the sampling area was previously described (Mukwaturi and Lin, 2015). After collection, the soil samples were oven-dried at 40 °C for two days in the laboratory and then ground with a mortar and pestle to pass through a 2 mm sieve. This is done to achieve a homogenous sample prior to analysis. Samples were later stored in an air-tight re-sealable laboratory polythene bags prior to the use in the experiment. Some major chemical characteristics of the soil samples are given in Table 1.

2.2. Experimental design

A triplicated batch experiment was conducted to observe changes in pH, Fe, Ca and As in the reacting solutions following mixing of a soil sample with an organic acid at a given concentration. All the three soil samples (M1, M2 and M3) mentioned previously were used and nine treatments were set for each soil sample. Three organic acids (citric acid, oxalic acid and malic acid) were selected and three concentration levels were set for each of them (Table 2). 150 mL plastic bottles were used as batch reactors. 10 g of each soil sample was placed into a bottle, followed by adding 50 mL of a relevant organic acid into the bottle. The loaded bottles were placed in a paper box after shaking each bottle by hand for 1 min. The experiment lasted for 14 days. pH of the reacting solutions was monitored during the period of the experiment by measuring solution pH on the 1st, 2nd, 3rd, 5th, 7th and 14th days of the experiment. The solution in each bottle was also sampled on two occasions (the 7th and 14th days of the experiment) for measurements of Fe, Ca and As. At each sampling occasion, 15 mL of the solution were taken from the bottle, placed into a centrifuge tube and then centrifuged at 3500 rpm for 10 min. The supernatant was further passed through a 0.45 μm membrane filter prior to analysis.

2.3. Laboratory analytical and statistical methods

For the initial soil characterization, pH and electrical conductivity (EC) of the soil samples were measured in a 1:5 (soil:water) extract using a calibrated Mettler Toledo 320 pH meter and a Mettler Toledo electrical conductivity meter, respectively. Total metal concentration was determined using a Niton XL2 Gold Handheld XRF Analyzer. The instrument was calibrated by firstly analysing the 73308 standard reference materials prior to sample analysis. To ensure accuracy and reliability of the results obtained, all analyses were performed in duplicates and the analysis time was set at 240 s. Soil organic matter content was determined using a Walkley-Black method. The pH in the solutions for the incubation experiment was measured using a Mettler Toledo 320 pH meter. Concentrations of Fe, Ca and As in the filtrate was determined using a Varian 720 ES inductively coupled plasma optical emission spectrometer (ICP-OES). Statistical analysis of the experimental data was performed using IBM SPSS software Version 13.0.

3. Results

3.1. Solution pH

The change in solution pH in various treatments during the entire period of the experiment is shown in Fig. 1. A higher dose generally resulted in a lower solution pH for any of the three LMWOA treatment groups (i.e. citric acid, oxalic acid and malic acid). There was a consistent trend showing that pH increased with increasing length of incubation time.

At the same molar concentration level (either 0.02 M or 0.05 M or 0.1 M), the solution pH for the three different LMWOA treatments was in the following decreasing order: malic acid treatment > citric acid treatment > oxalic acid treatment. All the three tested soil samples (M1, M2 and M3) had the same trend, as shown above (i.e. in the order of malic acid treatment > citric acid treatment > oxalic acid treatment). Solution pH tended to increase over time more sharply in the oxalic acid treatments than in either the citric acid treatments or the malic acid treatments, particularly in T1O (oxalic acid at a concentration of 0.02 M).

There was a high level of similarity in the temporal variation patterns among the three different soil samples. However, Sample M3 with an original higher soil pH (see Table 1) tended to have a higher solution pH, as compared to Samples M1 and M2 that had lower soil pH (see Table 1) though this trend was not always clear for all the treatments.

3.2. Extracted soil-borne Fe

The soil-borne Fe that was extracted in the 9 treatments on the 7th and 14th day of the incubation experiment is shown in Fig. 2. It is clear that on the 7th day, the variation pattern of extracted Fe was similar to each other for all the 3 soil samples used in the