



# Interactions of nano-oxides with low-molecular-weight organic acids in a contaminated soil



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## HIGHLIGHTS

- Low pH and the presence of citrate complexes enhanced metal mobility.
- Formation of oxalate surface complexes decreased metal leachability.
- Amorphous Mn oxide accelerated the stabilisation of Pb, Zn, Cu, Cd and As in soil.
- Nano-maghemite showed to be stable in low-molecular-weight organic acids.
- Amorphous Mn oxide was partly dissolved and secondary MnCO<sub>3</sub> precipitated.

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## ABSTRACT

Various low-molecular-weight organic acids (LMWOAs) play an important role in the mobilisation of contaminants and their subsequent uptake by plants. Nano-maghemite (NM) and an amorphous Mn oxide (AMO) were investigated for their stabilisation potential under simulated rhizosphere conditions in terms of their use during chemical stabilisation and aided phytostabilisation of metal(loid)s in contaminated soils. In order to understand the reactivity of these potential sorbents of contaminants in soils and subsequent mobility of metal(loid)s, a set of time-dependent batch leaching experiments was performed using a mix of acetic, lactic, citric, malic and formic acids simulating root exudates. Despite being relatively unstable under given conditions, the AMO proved to be an efficient amendment for rapid stabilisation of both metals and As compared to NM. Generally, low pH (~4) and the presence of citrate complexes resulted in higher mobility of metals in the non- and NM-amended soil. In contrast, the presence of AMO in the soil accelerated the neutralisation reactions related to pH increase and (co-) precipitation of secondary Fe/Mn/Al oxyhydroxides. Mineralogical transformations of the AMO showed to be crucial for contaminant immobilisation.

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## 1. Introduction

Synthetic oxides represent important sinks for metals/metalloids in soils through different immobilisation mechanisms including sorption, surface complexation or co-precipitation [1–4]. Therefore, engineered nano-oxides (particle size of tens to hundreds nm) represent promising amendments for soil remediation due to their high reactive surface areas and increased sorption capacities [e.g., 5]. Detailed investigations of the behaviour of these

potential stabilising amendments in soils are crucial for evaluating their efficiency and stability, especially in multi-element contaminated areas. Moreover, stable forms of contaminants lower the risk of their uptake by plants. In this context, the processes at the soil-root interface (i.e., in the rhizosphere) significantly affect the behaviour of both nano-sorbents and potential contaminants. Various organic compounds, including low-molecular-weight organic acids (LMWOAs), are exuded by plant roots as a response to a number of environmental stresses [6]. The release of organic acids is greatly plant-specific and results in modifications of the local rhizospheric physico-chemical conditions, such as pH, Eh or nature of soil organic matter [7,8]. Hence, LMWOAs could play a key role during the use of nano-oxides through their influence on

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**Table 1**  
Characteristics of the studied nano-oxides.

Oxide	Particle size (nm)	pH <sub>H<sub>2</sub>O</sub>	pH <sub>ZPC</sub>	BET surface (m <sup>2</sup> /g)
Maghemite <sup>a</sup>	20–100	3.0	3.1	46.6
AMO <sup>b</sup>	600–1200	8.1	8.3	14.8

<sup>a</sup> [11].

<sup>b</sup> [9].

metal/metalloid speciation and their mobility. Detailed research of the soil–LMWOAs–nano-sorbent interactions is missing, although necessary to understand contaminant mobility in the complex rhizospheric environment.

For this purpose, an Fe nano-oxide (maghemite,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) and a synthetic amorphous Mn oxide [9] have been investigated. The Mn-oxide has been prepared, characterised and tested as a potential stabilising amendment of contaminants in soils previously by Ettler et al. [10] and Michálková et al. [11]. The objectives of this study are (i) to assess the stability of nano-oxides in the presence of LMWOAs, (ii) to investigate the leaching behaviour of metal/metalloids from soil upon the interaction with LMWOAs and (iii) to assess the potential implications of nano-oxide behaviour for the immobilisation of metals/metalloids in soil under rhizospheric conditions.

## 2. Material and methods

### 2.1. Studied Fe/Mn nano-oxides

Two different nano-oxides were investigated (Table 1): (i) maghemite (NM;  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>; purchased from Sigma–Aldrich, Germany) and (ii) amorphous manganese oxide (AMO; synthesised according to Della Puppa et al. [9]).

### 2.2. Soil samples

Soil samples were collected in the vicinity of the Pb smelter at Přeboram (Czech Republic) from the upper layer (0–20 cm) of an agriculturally used soil. Soil pH was measured in a suspension with deionised water and/or 1 M KCl at 1:2.5 soil-to-liquid ratios (ISO 10390:1994). Total organic/inorganic carbon content (TOC/TIC) in soil was determined using the SSM-5000A analyser (Shimadzu, Japan) for solid samples. Bulk concentrations of major and trace elements were determined after decomposition in *aqua regia* (US EPA method 3051a) followed by microwave digestion (SPD-Discover, CEM, USA) and ICP-OES analysis (Agilent 730, Agilent Technologies, USA) (Table 2). The soil is classified as a Dystric Cambisol with 52% of silt, 35% of sand and 13% of clay.

### 2.3. Batch leaching experiments

A synthetic mixture of LMWOAs simulating root exudates (SRE) was used for a set of batch leaching experiments. The following mix of LMWOAs that are likely present in the rhizosphere was prepared: acetic, lactic, citric, malic and formic acids (molar ratio 4:2:1:1:1)

**Table 2**  
Bulk chemical composition and pH of the studied soil (values expressed as mean  $\pm$  standard deviation,  $n = 3$ ).

Element	mg/kg	Element	mg/kg
K	2374 $\pm$ 844	Cu	21.2 $\pm$ 1.3
Mg	2404 $\pm$ 319	Cd	6.39 $\pm$ 0.32
Ca	3674 $\pm$ 438	Pb	1577 $\pm$ 47
Mn	1626 $\pm$ 261	Zn	252 $\pm$ 30
Fe	18490 $\pm$ 1395	As	123 $\pm$ 5.8
Al	20201 $\pm$ 4885	TOC <sup>a</sup>	2.16 $\pm$ 0.04
pH <sub>H<sub>2</sub>O</sub>	6.42 $\pm$ 0.02	pH <sub>KCl</sub>	5.47 $\pm$ 0.02

<sup>a</sup> TIC < detection limit.

with a total concentration of 10 mM according to the extraction method used by Feng et al. [12].

First, the stability of nano-oxides (without soil) was tested at a liquid-to-solid (*L/S*) ratio of 500 L/kg as a function of time (0.5, 1, 2, 6, 12, 24, 48, 192, 288 and 384 h) to assess both the first interaction and long-term behaviour of NM and AMO in LMWOAs. The pH of the initial solution (pH 2.90) was adjusted using NaOH (p.a.) to optimised pH 4.84 (preliminary defined pH value of the studied soil sample upon the interaction with SRE, i.e., an average value in the given time intervals) to better simulate the soil conditions and pH evolution with time. Despite different neutralisation capacities of NM and AMO, the same initial pH was used in order to see and further compare their different behaviour. A mass of 0.02 g of NM and AMO, respectively, was placed into each 15-mL centrifuge tube (separate batches for individual time intervals) and 10 mL of the fresh SRE (pH 4.84) was added. The suspensions were continuously agitated (200 rpm) in darkness to prevent degradation.

Similarly, time-dependent (0.5–48 h) sets of batch experiments were performed with soil samples. A mass of 2 wt% NM and AMO was separately mixed with the soil. An aliquot of each amended soil sample was watered with deionised water to maintain ~60–70% of water holding capacity for one month (soil samples entitled I3-NM and I4-AMO accordingly). Amended soil samples without incubation (entitled I1-NM and I2-AMO) and non-amended soil samples (*P*) were tested for comparison. A mass of 2 g of dry soil (30 °C) was placed in a 50-mL centrifuge tube (separate batches for individual time intervals) and 20 mL of the fresh SRE (pH 2.90, without pH adjustment) was added to maintain *L/S* = 10 L/kg. The suspensions were kept in darkness to simulate the rhizosphere environment and continuously agitated. Time intervals were selected both to investigate the rapid reactions and to reach pseudo-equilibrium conditions in the studied system.

All experiments were run in triplicates with procedural blanks. After the experiments, physico-chemical parameters (pH, Eh) were measured immediately. The pH was determined using an inoLab<sup>®</sup> pH metre (pH 7310, WTW, Germany) equipped with a combined pH electrode (SenTix<sup>®</sup> 41, WTW, Germany). Redox potential was measured using a digital multimetre (Multi 3420, WTW, Germany) equipped with a combined IDS electrode (SenTix<sup>®</sup> ORP 900, WTW, Germany). All the experiments were performed at 24  $\pm$  2 °C.

The nano-oxide suspensions were centrifuged at 9000 rpm and filtered through 0.22- $\mu$ m nylon syringe filters. The centrifugation and filtration efficiency of nanoparticles has been verified by testing 0.45- $\mu$ m, 0.22- $\mu$ m and nano-filters at different centrifugation levels and comparing the differences in Fe/Mn concentrations in the leachates (data not shown). Finally, the pore size of 0.22  $\mu$ m has been assumed optimal according to nanoparticle aggregation. The soil suspensions were centrifuged at 5000 rpm and filtered both through 0.45- $\mu$ m and 0.22- $\mu$ m nylon syringe filters.

### 2.4. Analytical determinations and geochemical modelling

Leachate samples from each experiment were analysed for Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Si, Sr, Ti and Zn using ICP-OES (Agilent 730, Agilent Technologies, USA). Major inorganic (F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup>) and organic (lactate, acetate, propionate, formate, butyrate, malate, tartrate, maleate, oxalate and citrate) anions were determined using ion-exchange chromatography with suppressed conductivity (ICS 1600, Dionex, USA) equipped with IonPac AS11-HC (Dionex, USA) guard and analytical columns. Total dissolved organic/inorganic carbon (DOC/DIC) was determined using the carbon analyser TOC-L CPH (Shimadzu, Japan).

Leached solid residues of the AMO and NM were dried at 40 °C and prepared for X-ray diffraction (XRD) analysis (PANalytical X'Pert Pro diffractometer with X'Celerator detector; Cu K $\alpha$

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