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The pH-dependent long-term stability of an amorphous manganese oxide in smelter-polluted soils: Implication for chemical stabilization of metals and metalloids

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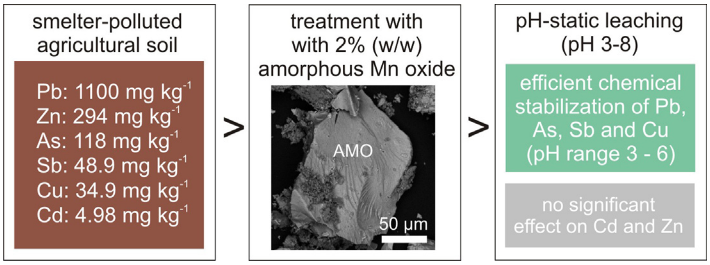
HIGHLIGHTS

- The stability of amorphous manganese oxide (AMO) is pH-dependent.
- "Labile" Pb, As and Sb decreased after treatment of a polluted soil with AMO.
- Efficient chemical stabilization of Pb, As, Sb and Cu, no effect on Cd and Zn.
- Most efficient contaminant retention under acidic conditions.
- Increase in chemical stabilization with time (6 months > 2 months of incubation).

GRAPHICAL ABSTRACT



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ABSTRACT

An amorphous manganese oxide (AMO) and a Pb smelter-polluted agricultural soil amended with the AMO and incubated for 2 and 6 months were subjected to a pH-static leaching procedure (pH 3–8) to verify the chemical stabilization effect on metals and metalloids. The AMO stability in pure water was pH-dependent with the highest Mn release at pH 3 (47% dissolved) and the lowest at pH 8 (0.14% dissolved). Secondary rhodochrosite ($MnCO_3$) was formed at the AMO surfaces at pH > 5. The AMO dissolved significantly less after 6 months of incubation. Sequential extraction analysis indicated that "labile" fraction of As, Pb and Sb in soil significantly decreased after AMO amendment. The pH-static experiments indicated that no effect on leaching was observed for Cd and Zn after AMO treatments, whereas the leaching of As, Cu, Pb and Sb decreased down to 20%, 35%, 7% and 11% of the control, respectively. The remediation efficiency was more pronounced under acidic conditions and the time of incubation generally led to increased retention of the targeted contaminants. The AMO was found to be a promising agent for the chemical stabilization of polluted soils.

1. Introduction

Iron and manganese oxides are often tested for chemical stabilization of metals and metalloids in polluted soils mainly due

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Table 1
Properties of the studied smelter-polluted agricultural soil.

Code	Units	Value	Code	Units	Value
pH	std units	5.32	As	mg kg^{-1}	118 ± 2
CEC	cmol + kg^{-1}	6.96	Cd	mg kg^{-1}	4.98 ± 0.02
C_{org}	%	1.79	Cu	mg kg^{-1}	34.9 ± 1.4
S_{tot}	%	0.02	Sb	mg kg^{-1}	48.9 ± 0.59
P_{tot}	g kg^{-1}	2.42	Pb	mg/kg	1100 ± 19
			Zn	mg kg^{-1}	294 ± 7
Particle size distribution			Mn	mg kg^{-1}	1830 ± 101
Sand	%	57.3	Fe	mg kg^{-1}	20800 ± 990
Silt	%	32.7			
Clay	%	10.0			
Oxalate extractable					
Fe	g kg^{-1}	2.61			
Al	g kg^{-1}	1.20			
Mn	g kg^{-1}	1.21			

to their sorption potential, which leads to a decrease in contaminant mobility and bioavailability [1–4]. Comparison of the sorption efficiencies indicated that Mn-oxides can be much more efficient sorbents than Fe-oxides for some metals (e.g. Pb) [5,6]. Moreover, Mn oxides, through their dissolution, can change the redox speciation of contaminants, leading to their oxidation, which is not favorable in the case of Cr (Cr^{III} to more mobile and toxic Cr^{VI}) [7–10], but can be suitable for As (As^{III} oxidizes to less mobile and less toxic As^{V}) [11–17].

Recently, a novel amorphous manganese oxide (AMO), prepared by a modified sol-gel procedure generally used for the birnessite synthesis but without the heating step, was tested as a new sorbent for metals and its sorption efficiency was found to be comparable with that of birnessite [18]. Despite the fact that 10–18% of AMO dissolved during the 90 days of exposure in contrasting soils, it was concluded that it is relatively stable and can be potentially used as an amendment for polluted soils [19]. The first experiments studying the chemical stabilization of Cd, Cu and Pb in polluted soils using AMO indicated that the adsorption capacity of AMO was an order of magnitude higher than those recorded for selected Fe-nanooxides (nano-maghemite, γ-Fe_2O_3 and nano-magnetite, Fe_3O_4) [20].

The influence of varying environmental conditions (where pH is the major driving force) on chemically stabilized metal(loid)s in soils is often overlooked in evaluation of the efficiency of a particular remediation technique. The adsorption efficiency of the AMO in soils is expected to be highly dependent on the pH and time of aging. For these reasons, the present study investigated (i) the AMO stability in aqueous environments as a function of the pH and liquid-to-solid (L/S) ratio used during the leaching experiments and (ii) the changes in chemical fractionations of inorganic contaminants and their pH-dependent leaching from an AMO-amended smelter-polluted agricultural soil.

2. Experimental

2.1. Amorphous manganese oxide and studied soil

The synthesis of a poorly crystalline or amorphous manganese oxide (AMO) was based on the methodology of Ching et al. [21], generally used for birnessite synthesis, but without the heating step (details of the procedure are given in [18,19]). The specific surface area (SSA) of the AMO was measured by BET measurement using a Sorptomatic 1990 Thermo Electron instrument (Thermo Fisher Scientific, USA) and corresponded to 14.8 $m^2\,g^{-1}$ (without degassing) or 157 $m^2\,g^{-1}$ (after degassing at 110 °C). The average oxidation state of Mn was 2.52 (corresponding to the chemical formula $MnO_{1.26}$) [18]. The natural pH of AMO was obtained by acid neutralization capacity/base neutralization capacity measurement (ANC/BNC; details see below) and corresponded to 7.12 (Fig. S1 in the Supplementary Material). The granulometry of the AMO sample used in the present study was measured using a Sympatec particle size analyser equipped with a HELOS laser diffraction sensor and ultrasound sample treatment (Sympatec GmbH, Germany) and yielded the following results: <1 μm (3.28%), 1–2.6 μm (22.01%), 2.6–5 μm (34.25), 5–10 μm (28.69%) and >10 μm (11.77%). Previous investigations using X-ray diffraction (XRD) and scanning electron microscopy (SEM) indicated that small contents of Mn-oxalate hydrate can be present in the AMO as a result of glucose transformation used during the synthesis [19].

An agricultural soil (classified according to US Soil Taxonomy as Inceptisol Typic Dystrudepts) was used as a model soil for chemical stabilization experiments. The soil was polluted by emissions from a Pb smelter located in Příbram (Czech Republic) and was previously studied by [22]. The soil properties and main physicochemical parameters are reported in Table 1.

2.2. Amorphous manganese oxide leaching

The pH-dependent stability of AMO was tested using a pH-static leaching experiment according to the European standard CEN/TS 14,997 [23]. Preliminary determination of steady-state pH and the acid and base consumptions (ANC/BNC) was performed before the pH-static leaching using manual titration and pH measurement every 30 min. The pH-static experiments were carried out at 20 ± 4 °C for 48 h. A mass of 1 g of solid was placed in a 20 mL centrifuge PP bottle and 9.6 ml of MilliQ+ deionised water were added to maintain an L/S ratio of 9.6 with a final ratio of about 10 after addition of the acid/base. Six pH values between 3 and 8 at 1-unit increments were selected to represent the pH range relevant for soil environments. Acid (14 M, 1 M or 0.1 M HNO_3) or base (5 M, 2 M or 1 M NaOH) was added to adjust the pH values. A variant conducted at the natural pH (i.e., without acid/base addition) was included in all cases. The reactors were agitated continuously (except for the time of pH control and titration). After 48 h, the suspended solids were allowed to settle for about 10 min and the physical-chemical parameters (pH, Eh, specific conductivity) were measured immediately using Schott multimeters (Schott Instruments GmbH, Germany) in the leachate before filtration (Millipore® 0.45 μm). All the experiments were performed in duplicate and included procedural blanks.

To evaluate the effect of the L/S ratio on AMO dissolution, leaching in deionized water (natural pH) was performed at L/S ratios