

# STABILITY AND IMMOBILIZING POTENTIAL OF NOVEL SURFACE-MODIFIED AMORPHOUS MANGANESE OXIDE

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## Introduction

A novel stabilizing agent, so called amorphous manganese oxide (AMO), was synthesized (Della Puppa et al., 2013) and successfully tested for stabilization of both metallic (Cd, Cu, Pb, Zn) and metalloid (As) species in contaminated soils (Ettler et al., 2015; Michálková et al., 2014; Michálková et al., 2016). Yet, the increased dissolution of the phase, especially in conditions of low pH, connected with unwanted oxidation of soil organic matter (SOM) was observed. On the other hand, a layer of MnCO<sub>3</sub> has been found to form on the surface of AMO particles when incubated in soils, increasing their stability and lowering the SOM dissolution (Ettler et al., 2014; Michálková et al., 2014). For that reason, a surface-coverage of AMO particles with MnCO<sub>3</sub> was proposed to optimize the properties of this stabilizing agent.

## Methods

An amorphous manganese oxide (AMO) was synthesized according to Della Puppa et al. (2013). The surface-modified AMO (Sm-AMO) was subsequently prepared by incubating the material in deionized water saturated with CO<sub>2</sub>. For each batch, 3 g of AMO were mixed with 30 mL of deionized water and placed in 50 mL burette. The CO<sub>2</sub> was evolved by dropping the diluted HCl onto NaHCO<sub>3</sub> (30 g of NaHCO<sub>3</sub> per each batch), captured and conducted into the AMO suspension. After the end of the reaction, the burettes were closed tightly. This procedure has been repeated in another three consecutive days and on the fifth day, particles were filtered and air-dried. Identification of the solid phases was performed using X-ray diffraction spectrometry (XRD) together with scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS).

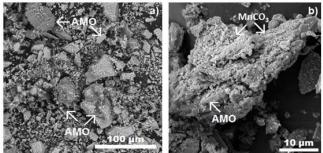
Incubation batch experiments were performed to investigate the stability and transformations of AMO and Sm-AMO particles together with their influence on soil solution characteristics and mobility of metal(loids). The experiment was conducted in two variants using two contaminated soils: Fluvisol contaminated with As, Cd, Pb and Zn and Leptosol contaminated with As. Firstly, to examine the possible transformations and stability of AMO/Sm-AMO particles, 1 g of AMO/Sm-AMO was placed into two-layered sealed polypropylene poach. Poaches were placed into plastic pots together with 150 g of soil. Rhizon samplers enabling the collection of the soil solution were placed below poaches. Secondly, soil in

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variants: C (control) and AMO/Sm-AMO mixed with soil at concentration of 1% (w/w) was placed into plastic pot with Rhizon sampler. All pots (i.e., with and without poaches) were maintained at ~60-70% for 1, 2, 4 and 10 weeks. After these periods, the soil solution was collected. The pH, Eh, content of metals/metalloids and DOC (dissolved organic carbon) in soil solutions together with the weight loss of AMO/Sm-AMO particles were determined.

#### Results

The XRD together with the SEM/EDS confirmed the presence of MnCO<sub>3</sub> layer on the surface of Sm-AMO (Figure 1). On the basis of metal(loid) concentrations in soil solution, both materials proved efficient in decreasing concentration of all risk elements in soil



**Figure 1.** AMO particles (a) and Sm-AMO particles (b) covered with MnCO<sub>3</sub> layer (SEM image).

solution. For example, the concentration of Zn in soil solution was decreased more than five times compared to control after 10 weeks. Almost no significant differences between the stabilizing efficiency of AMO and Sm-AMO were recorded. The amount of leached Mn from amended soils was more 20 times higher than in the case of control, yet the concentrations recorded for AMO and Sm-AMO were not statistically different. Interestingly, despite the comparable amounts of dissolved Mn, the weight loss was significantly lower (about 50%) in the case of Sm-AMO in all time intervals increasing in time from  $\sim 1.6\%$  in 1 week to  $\sim 9.4\%$  in 10 weeks.

### Conclusion

The Sm-AMO was successfully prepared and its stabilizing efficiency towards risk elements was comparable to that of the AMO. The weight loss of the Sm-AMO was significantly lower than of AMO.

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