



## **Mobilization of As-containing Colloids by Liming?**

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The management of Pb- and As-contaminated shooting range sites often includes liming in order to reduce the mobility of heavy metals in soils. The liming-induced pH-increase is meant to immobilize dissolved cations and thus prevent Pb leaching into deeper soil horizons and groundwater (EPA, 2001). However, recent studies showed a pH-increase enhances the release and stability of colloids and may thus contribute to a mobilization of colloid-associated metals.

Whilst the behaviour of dissolved Pb in response to liming (Turpeinen et al., 2000) as well as the affinity of Pb for colloids (Jensen et al., 1999) is well documented, investigations for dissolved and colloid-associated As are scarce. According to the state of the art, pH increase might induce an increase in dissolved As due to a desorption from sesquioxides (Smith et al., 1998). On the other hand, increasing pH might produce new sorption sites, e.g. by the dispersion of As-sorbing colloids. In the presence of polyvalent cations, the pH increase might induce the formation of cation bridges. Besides, the impact of a pH-change and counterion valency on colloid generation and stability as well as possible interactions with As may vary greatly with Corg- and sesquioxide-content of the soil.

The aim of our work is to investigate the influence of a pH-increase on the mobilization of dissolved and colloid-associated As under special consideration of the role of the counterion in a sesquioxide-rich and an organic-rich soil.

We conducted batch experiments using top soil samples of a mineral (pH 5) and an organic soil (pH 4) of former shooting range sites. The pH of the suspensions were increased to pH ranges between 6 and 7 by adding either a monovalent base (KOH) or a divalent base (Ca(OH)<sub>2</sub>). Differences in ionic strength of the treatments were compensated by adding a background electrolyte solution. A control batch was shaken

with KNO<sub>3</sub>- or Ca(NO<sub>3</sub>)<sub>2</sub>-solution, respectively. The filtered suspensions (1.2 μm) were analyzed for As, Al, Fe, Mn, and Corg. Besides, turbidity, zeta potential, and particle size were determined. Colloidal fractions were separated by means of multi-stage tangential ultrafiltration and ultracentrifugation, respectively.

In the mineral soil, our findings of the KOH-treatment conflict with indications in the literature: concentrations of dissolved As decreased, whereas concentrations of colloid-associated As increased. In the presence of a divalent cation (Ca), both dissolved and colloidal As concentrations decreased and were lower than in the presence of the monovalent cation (K). Results revealed an increase in the amount of mobilized colloids with increasing pH, with the increase being much stronger with K than with Ca as a counterion. In the presence of K, As was found to be associated with colloidal sesquioxides. The presence of the Ca ion caused a suppression of the dispersion of sesquioxides and colloidal As was no longer detectable.

In the organic-rich soil, dissolved As concentrations increased with increasing pH in the presence of the monovalent cation. These findings are in line with results reported by the literature (for instance Smith et al., 1998). A pH-increase together with the addition of a divalent cation, however, lead to a decrease in dissolved As concentrations. Arsenic was not found to be associated with colloids in the presence of Ca<sup>2+</sup>. The amount of mobilized colloids in response to a pH-increase showed similar results to the mineral soil. In case of both counterions, the zeta potential was getting increasingly negative with increasing pH. The charge increase in the presence of the Ca ion is offset in comparison to the K ion.

Our present results indicate the increase in pH of mineral soils causes a reduction of dissolved As concentrations, either by increasing the availability of sorption sites due to micro-aggregate dispersion (K-treatment) or by flocculation (Ca-treatment). In contrast, the effect of increasing pH on the mobilisation of colloidal As strongly depends on the valency of the dominating cation. Similarly, in the organic-rich soil, pH-induced mobilisation of As-containing colloids occurs only if monovalent cations are dominant. The valency of the cation controlled dissolved As concentrations but had no impact on the formation of As-containing colloids as might have been assumed by “bridging” of Ca between a negatively charged colloid and As anion. In the context of a liming-induced pH increase our results suggest the mobilization of colloidal As to be of no relevance as long as divalent cations are dominant.

Environmental Protection Agency 2001. Jensen, DL, Ledin A, and Christensen TH 1999 *Wat. Res.* 33, 2642 -2650. Smith, E, Naidu R and Alston AM 1998 *Adv in Agron* 64, 149-195. Turpeinen, R, Salminen J, and Kairesalo T 2000 *Environ. Sci. Technol.* 34, 5152 - 5156.